KINETICS OF SOME FAST REACTIONS

I. Reaction of Sodium Hypochlorite and Sodium Sulfite
II. Reaction of Carbondioxide and Diethanolamine

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By
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CERTIFICATE

Certified that the work 'KINETICS OF SOME FAST REACTIONS:(1) Reaction of Sodium Hypochlorite and Sodium Sulfite; (2) Reaction of Carbondioxide and Diethanolamine' has been carried out under my supervision and that the work has not been submitted elsewhere for a degree.

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CONTENTS

KINETICS OF SOME FAST REACTIONS

(1) Reaction of sodium hypochlorite and sodium
    sulfite

(2) Reaction of carbondioxide and diethanolamine

ABSTRACT

The kinetics of some fast homogeneous liquid phase
reactions have been studied by a flow thermal method. This
method eliminates the effects of diffusion, and provides a
technique for the study of fast homogeneous reactions.

The kinetics of the reaction of sodium hypochlorite
with sodium sulfite have been studied. The search of the
literature indicates that Lister and Rosenblum [6] were the
only one to study the kinetics of this important reaction.
The present studies indicate that the reaction takes place
between hypochlorite and sulfite ions and is second order.
The second order rate constant at $30^{\circ}C$ and activation
energy are 6750 (lit)/(gmole)(sec) and 15.6 k.cal/gmole,
respectively.

A study of the carbondioxide-diethanolamine was also
made, for which many diverse kinetics have been reported
in the literature. Results indicate that the reaction is
complex. A reaction scheme is proposed. The overall second
order rate constant at $30^{\circ}C$ and activation energy are found
to be 1823 $(gmole/liter)^{-1}(sec)^{-1}$ and 12.41 k.cal/gmole,
respectively. Results are compared with the work of several
other investigators.

SECTION 1

REACTION OF SODIUM HYPOCHLORITE AND SODIUM SULFITE

CONTENTS

NOMENCLATURE

A	sulfite concentration, gmoles/liter
A_0	initial concentration of sulfite, gmoles/liter
B_0	initial concentration of hypochlorite, gmoles/liter
K''	second order rate constant, $(\frac{g\ mole}{liter})^{-1}(sec)^{-1}$
M	concentration, gmoles/liter
T	absolute temperature, $^{\circ}K$
θ	time, sec.

RUNS

RH	effect of hypochlorite
RS	effect of sulfite
RT	effect of temperature

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CHAPTER 1

INTRODUCTION

1.1 General

Chlorine is widely used as a bleaching agent and for bacterial control in the pulp, paper, beverage, canning and other food processing industries. Sodium hypochlorite, called soda bleach liquor, is most widely used in pulp and textile industries for bleaching purposes. Chlorine is also added in power plant cooling water streams in order to keep condenser tubes free of slime.

After its use, chlorinated water containing significant amount of hypochlorous acid is returned to the local stream or estuary where it is threat to aquatic life. This threat can be removed by injecting sulfurous acid or sodium sulfite solution in outgoing streams leading to oxidation-reduction reaction

$$Cl^- + SO_3^{--} \longrightarrow Cl^- + SO_4^{--} \qquad (1)$$
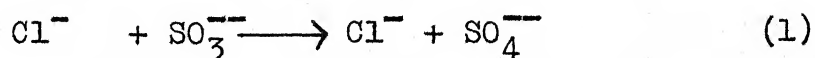
In a well buffered stream this process does nothing more than increase the sulphate and chloride ion concentration. Thus, the study of the kinetics of this important reaction would be very much helpful to control the pollution due to hypochlorous acid.

1.2 Literature survey

Experimental treatment of municipal water by excess chlorine (and dechlorination with sulphur dioxide) for taste and odor destruction was reported in 1912 and again in 1925 by Sir Alexander Houston [1]. Presently, most of the water supply plants in the world are using chlorine for bacterial control. In a recent paper, Sadek et al. [2] discussed the use of chlorine-sulphur dioxide reaction in the aqueous phase in connection with the control of sulphur dioxide emissions from the Hargreaves process. Chlorine was dissolved in the water producing hypochlorous acid and hydrochloric acid.

$$Cl_2 + H_2O \longrightarrow HClO + HCl \qquad (2)$$
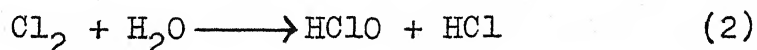
Sulphur dioxide was also dissolved in water producing bisulfite and sulfite ions in the solution. These ions reacted with hypochlorous ions to produce sulphuric acid and hydrochloric acid.

Berker and Whitaker [3, 4] also discussed that the same reaction can be used for the control of unwanted chlorine emissions which occur in power plant cooling water streams. In order to keep condenser tubes free of slime, chlorine is periodically dissolved in the cooling water stream yielding hypochlorous and hydrochloric acid.

Thus, the greatest single outlet for chlorine in industrial water treatment is in the control of bacterial, algae, slime,

and macroscopic biological fouling organisms in fresh water and saline condenser cooling waters. For control of slimes, tubercles, and the spot or larvae stages of larger organisms, free residual chlorine concentrations in the order of 0.5 to 2 m.g/liter are often employed [5].

The design of dechlorination units requires knowledge of the kinetics indicated by equation (1), as does the control of sulfur dioxide emission. Although apparently unknown in the chemical engineering literature, the kinetics have been studied by Lister and Rosenblum [6]. They used rapid flow technique and absorbance of solution was measured by means of a spectrophotometer. This was the first study of the kinetics of this reaction and a careful search of the literature reveals that it is currently the only such study. Lister and Rosenblum [6] reported that the overall reaction was second order.

1.3 Present work

In this investigation, measurements were made of the reaction rate of hypchlorite and sulfite by the flow thermal method of Hartridge and Roughton [7]. The principle involved the measurement of the temperature change due to reaction. The degree of conversion was calculated from this temperature change and the known heat of reaction.

CHAPTER 2

EXPERIMENTAL APPARATUS AND PROCEDURE

2.1 Materials

The prime materials used herein were sodium hypochlorite and sodium sulphite. These chemicals were obtained from Jay Ravik Chemicals (INDIA), and J.T. Baker Chemical Co., N.J. (U.S.A.), respectively.

2.2 Apparatus:

Rapid-mixing continuous flow method of Hartridge and Roughton [7] was used for the present study. The general schematic diagram of the experimental set-up is given in Figure 1. The basic features of the equipment are similar to that used by Srivastava et al. for study of sulfite and dithionite oxidations [8,9,10,11]. The main elements of the overall set-up are the storage tanks, thermostatic bath, flow control valves, flow meters, mixer and an observation tube. The set-up was designed to fulfil following capabilities and characteristics.

1. The temperature of the thermostatic bath can be controlled to within $\pm 0.1^{\circ}C$

2. The flowrate can be controlled to vary less than 1 per cent

3. Mixing is extremely rapid
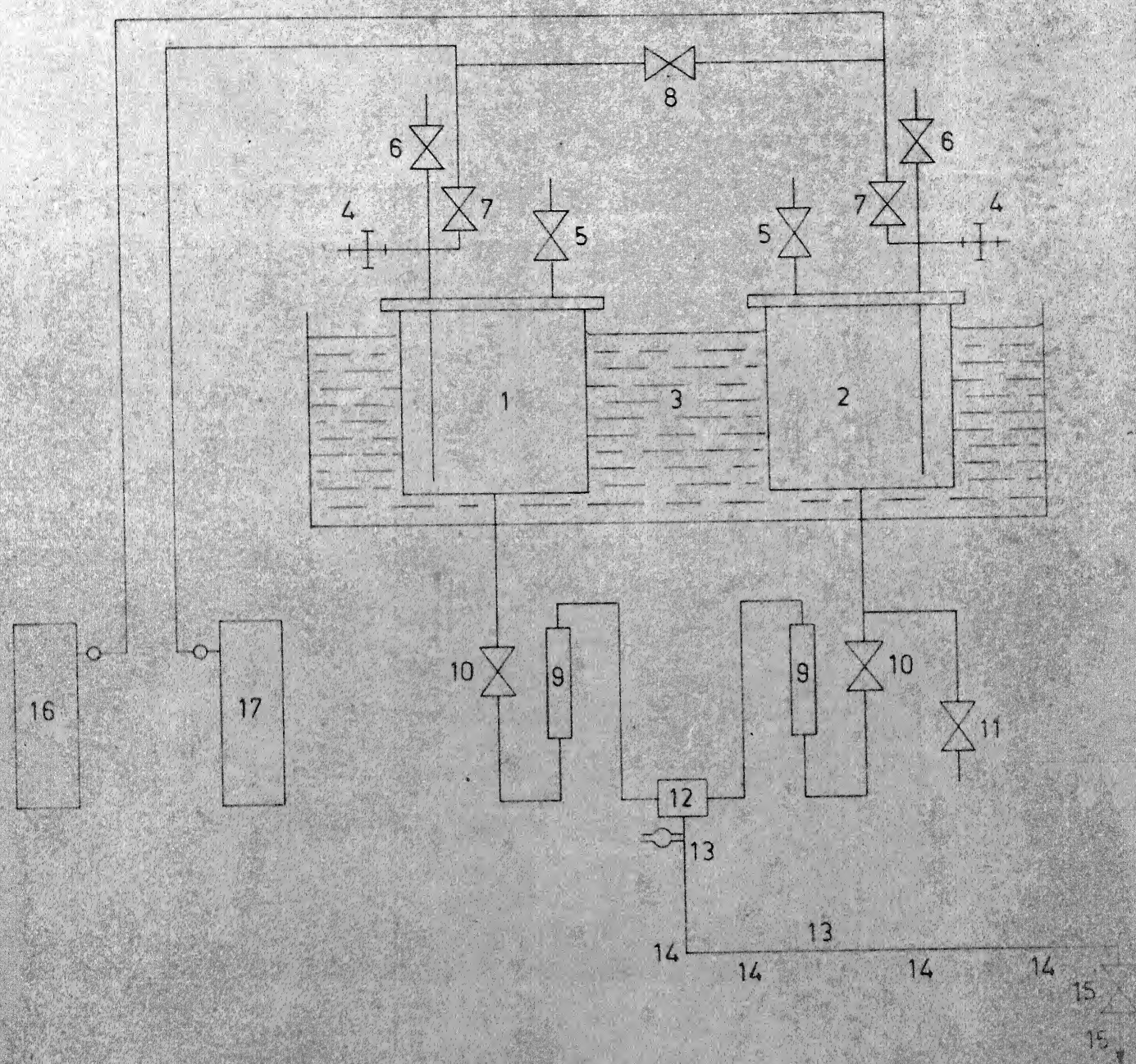
Fig 1 Flow diagram of experimental set up

Key to Figure 1

1 and 2	Reactant solution feed tanks
3	Constant temperature water bath
4	Safety valve
5	Vent valve
6	Reactant solution feed valve
7	Gas feed valve
8	Needle valve
9	Rotameter
10	Flow control valve
11	Sample tap
12	Mixer
13	Thermocouple
14	Observation tube
15	Desorption control valve
16 and 17	Gas supply cylinders

4. Output response from the thermocouples is
   measured by means of a quick response and
   good stability microvoltmeter (Keithley Model
   149 Microvoltmeter)

5. Flow in the reactor can be made steady by
   pressurizing the tanks

6. Increased concentration of a water soluble
   gas can be obtained by operating the system
   at elevated pressure, if desired.

2.3 Storage tanks

Two storage tanks were fabricated from 316 stainless
steel. Each tank with a capacity of 6 liters was used to
store and supply the feed solution. Nitrogen was used to
pressurize the tanks and to stirr the solutions, occasionally,
by bubbling the gas through the tank. The tanks were provided
with a pressure tight flange at the top with two holes fitted
with 3/8 inch valves and fittings, one for charging the feed
solution and gas, and other for venting. Safety valves were
provided at the top of the storage tanks. Both the tanks
were kept in a constant temperature water bath.

The arrangement was made to connect two storage tanks
either with only one gas cylinder or with two gas cylinders,
containing two different gases.

The bottom of the storage tanks were connected by 3/8
inch o.d. stainless steel tubes which were provided with

control valves. This was again connected to the inlets
of the mixing chamber via flow meters. These tubes were
wrapped with two inches of fiberglass and asbestos insulation
to minimize heat transfer to the surroundings.

2.4 Constant temperature control

Constant temperature water bath was fabricated from
brass and was used to maintain a constant temperature for
both storage tanks. A Jumo-German contact thermometer, $0-100^\circ C$,
connected to a relay device was used to control the tempera-
ture to an accuracy of $\pm 0.1^\circ C$. A Remi-stirrer was used to
stirr the water in the bath.

2.5 Flow rate measurements

The flow rates of the solutions were measured by means
of Gilmond flow meters. The two flow meters provided a flow
range of 0 to 16 ml per second and 0 to 35 ml per second.
Both the flow meters were calibrated prior to the actual
runs. The accuracy of the flowmeters was ± 1 per cent of
full scale.

2.6 Observation tube

The observation tube was made of plexiglass tubing of
1/4 inch o.d. by 1/8 inch i.d. It was connected to the mixing
chamber by means of a plastic male connector. Along the
length of the observation tube, a number of positions were
provided to locate the thermocouples. The outlet of the

observation tube was connected to a 3/8 inch drain line through a needle valve to control the desorption of the dissolved gas, if any. Whole tube was insulated with two inches of fiberglass and asbestos insulation to minimize heat transfer to the surroundings.

2.7 Mixing chambers

The mixer was made of a 4" x1" x1" block of plexiglass. The two fluid streams entered the mixing chamber in opposite direction through 3/8" to 1/8" reducers as two jets. Mixing was completed in an entremely short time due to turbulence created in the mixer. One outlet of the mixing chamber was connected to observation tube while the other was used to locate thermocouples at the mixing points. The mixer was insulated with approximately two inches of fiberglass and asbestos insulation.

2.8 Temperature measurements

The differential measurements of the temperature were made by means of pairs of thermocouples opposed in series to give increased response to the small temperature ranges. The thermocouples were made of 24 gauge copper and constantan wires. Four thermocouples were made and connected opposite in series. Each lead from the pair of thermocouple junctions was inserted in a 1/4 inch plexiglass tube which was then sealed with epoxy resin cement. The thermocouples were

calibrated against a 25 ohm Leeds and Northrup platinum
resistance thermometer and Muller bridge assembly. The
calibration curve is given in Figure 7, Appendix A. The
reliability of the equipment was checked using the NaOH-CO_2
system. The average of the second order rate constant agreed
within 5 per cent with the value reported by Pinsent et al.[12].

2.9 Experimental procedure

Sodium hypochlorite solution was made by diluting the
known amount of hypochlorite solution with distilled water,
and was charged to tank 1. Sodium sulphite solution of
desired concentration was also made in distilled water, and
was charged to tank 2. Both the solutions were allowed five
to six hours to attain temperature equilibrium. The solutions
were occasionally stirred with nitrogen. Microvoltmeter was
stabilized by turning it on half an hour before taking readings.

When both the feed tanks attained temperature equilibrium,
the tanks were pressurized by nitrogen to 50 psig to obtain
a steady flow in the reactor. Firstly, each solution was
allowed to pass separately in order to set the microvoltmeter
to zero reading with the help of zero suppress knobs. This
accounted for any temperature change due to friction or heat
transfer to the surroundings. Then, both the solutions were
allowed to pass, at known flow rates, to measure the actual
voltage rise due to reaction occurred. A steady value of
differential e.m.f. from the thermocouples located at the

mixing points and a point along the observation tube was obtained within seconds on the microvoltmeter.

Just prior to each run, both the solutions were analysed by standard titration methods [13]. The hypochlorite solutions were analysed in the following way. A standard solution of potassium iodide was made in distilled water. An excess amount of this solution was acidified with glacial acetic acid and then it was reacted with a known amount of sample taken out from tank 1. The reaction was allowed to occur for 10 minutes in a dark place. The liberated iodine was then titrated with a standard sodium thiosulphate solution using starch solution as an indicator. From this titration the amount of hypochlorite in the solution was readily calculated.

Sodium sulfite of the desired concentration, determined by titration to the neutral point with alkaline iodine-iodide solution [13], was charged to the other tank.

CHAPTER 3

RESULTS AND DISCUSSION

The experimental data for the runs have been presented in Appendix B.

The energy liberated by the reaction raised the temperature of the solution and total temperature rise was measured for each residence time. The change in sulfite concentration, M, was measured by the energy balance $H_R \times M = T \times C_p$. The mean heat capacity, C_p, of the solution was taken as that of water since the concentrations of both the reacting solutions were very low.

Figure 2 shows the plots of temperature difference as a function of residence time in two typical runs (RH-1 and RH-7). Such plots showed straight lines with different slopes for short residence times and then some curvature as the reactants are consumed. Such type of lines existed in all the runs. The rate of reaction was calculated from the heat of reaction and initial slope of such lines. A sample calculation is given in Appendix B.

The overall stoichiometry for the oxidation-reduction reaction is as follows:

$$NaClO + Na_2SO_3 \longrightarrow NaCl + Na_2SO_4 \qquad (3)$$
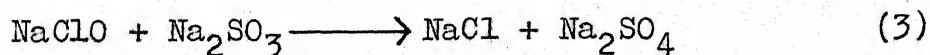
The standard enthalpy of the reaction is 81.3 k.cal/gmole of sulphite reacted [14, 15].
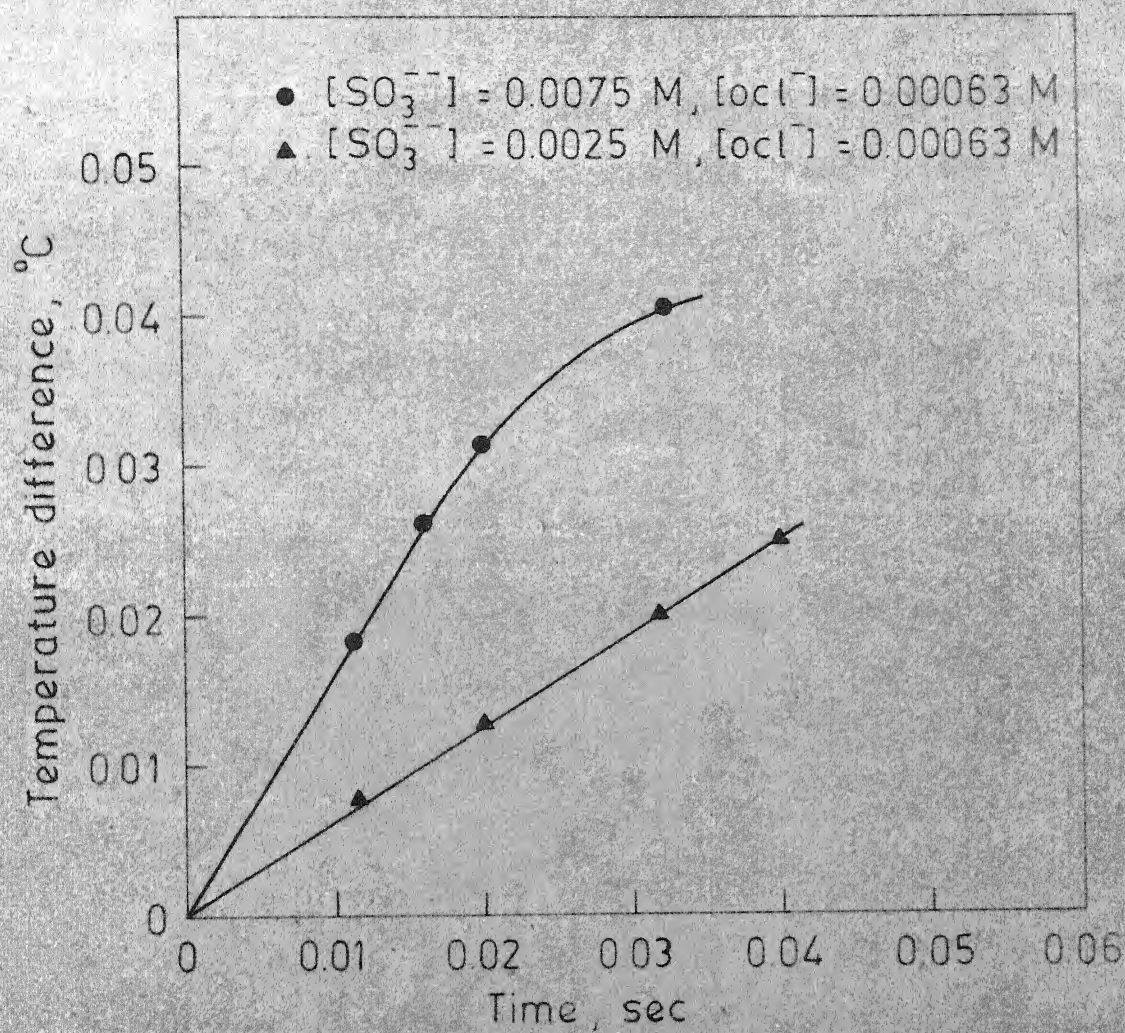
Fig 2 Typical temperature profiles as a function of time of reaction at 30 °C

3.1 Effect of hypochlorite concentration

A number of experiments were performed at various hypochlorite concentrations to investigate its effect on the rate of reaction. The rate data have been presented in Tables 1 and 2, Appendix B. All the experiments were conducted at $30^\circ C$. The concentration of hypochlorite was varied in the range 0.0006 M — 0.005 M. The concentration of sulfite was kept constant at 0.0025M and 0.0075M.

The rate of sulphite consumption is plotted as a function of average hypochlorite concentration. Figure 3 shows that the rate against hypochlorite concentration results in the one power relation for both the sulfite concentrations. Lister and Rosenblum [6] also found the one power relation with respect to hypochlorite for this reaction.

3.2 Effect of sulfite concentration

Tables 3 and 4, Appendix B give the rate data for the effect of sulfite concentration on the reaction rate. The reaction temperature for all the runs was maintained at $30^\circ C$. The concentration of sulfite was varied in the range 0.00125 M — 0.01 M. The concentration of hypochlorite was fixed at 0.00125 M and 0.00625 M.

The relation of rate versus sulfite concentration is shown in Figure 4. Figure 4 shows that the rate against sulfite concentration also results in the one power relation for both the hypochlorite concentrations used. The same relation was investigated by Lister and Rosenblum [6].
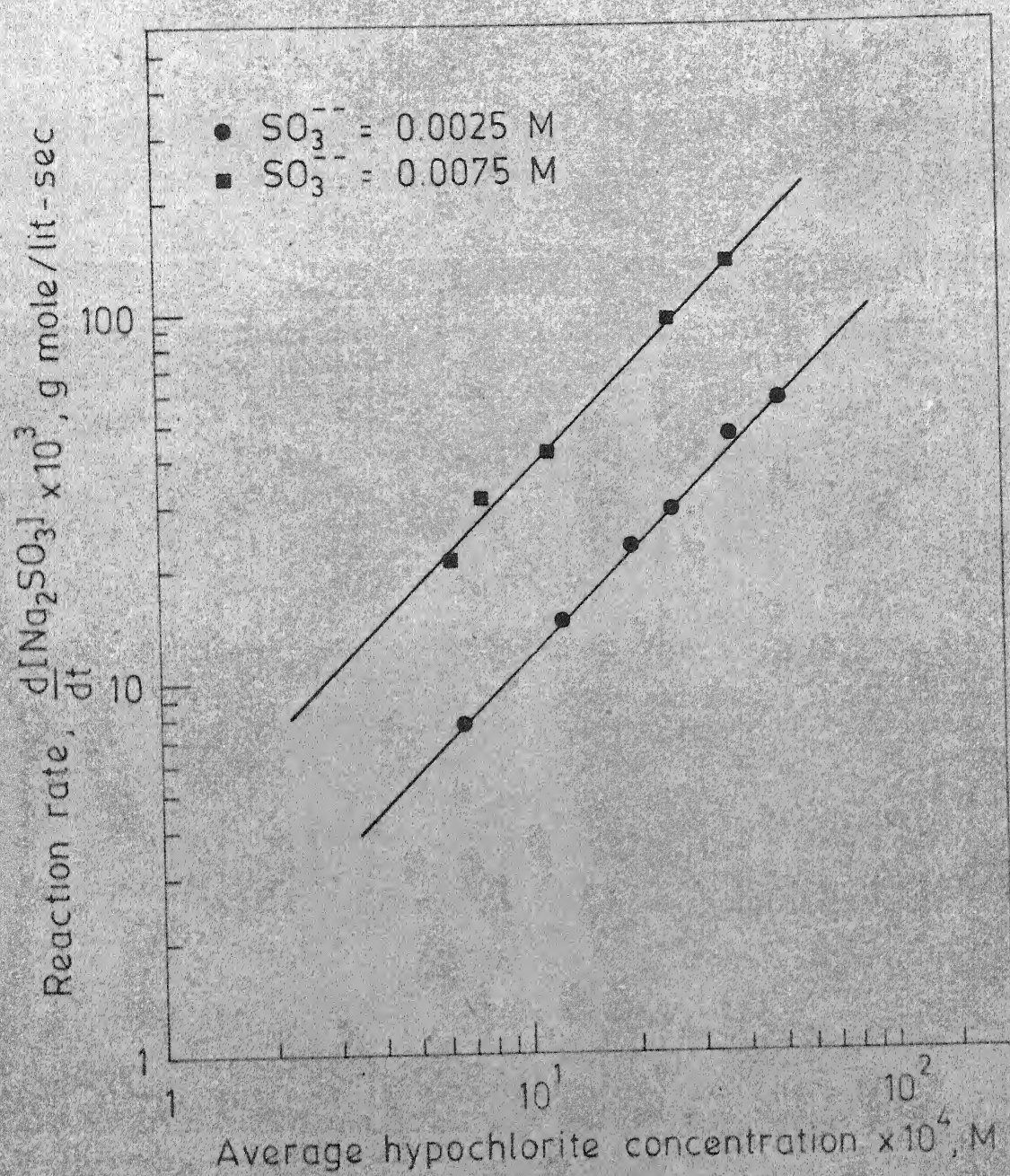
Fig 3 Effect of hypochlorite concentration on reaction rate at 30 °C
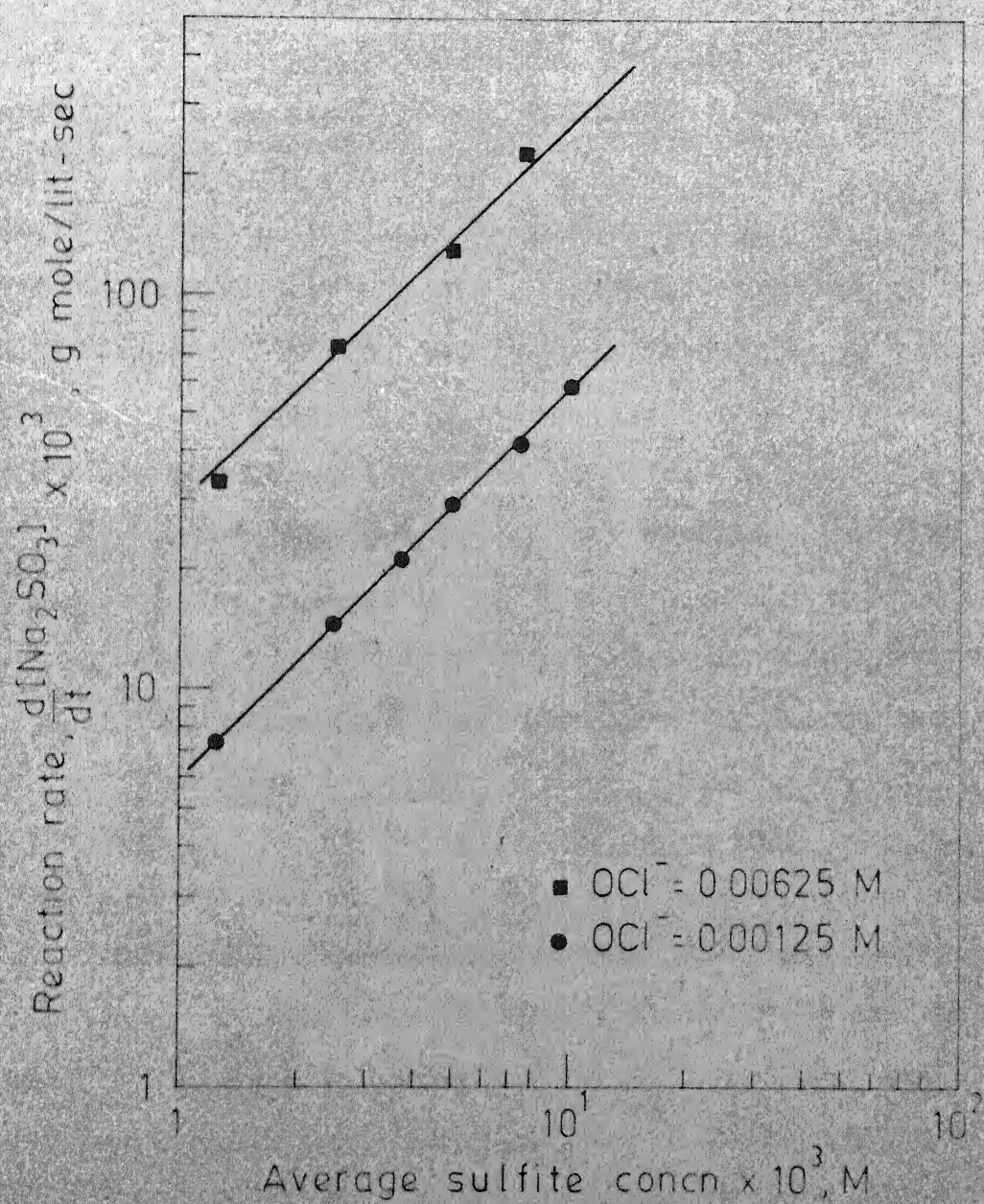
Fig 4 Effect of sulfite concentration on reaction rate at 30 °C

3.3 Kinetics

If the reaction between hypochlorite and sulfite is irreversible and second order, the following relationship should hold:

$$-\frac{2.303}{(B_O-A_O)}\left[\log\frac{A}{A+(B_O-A_O)}\right]_{A_O}^{A} = k'' \theta \qquad (4)$$

where A_O and B_O are initial concentrations of sulfite and hypochlorite, respectively, A is concentration of sulfite at any time θ and k'' is second order reaction rate constant. Thus in this case, a plot of the left hand side of equation (4) versus θ should give a straight line.

An exhaustive number of runs were made at five residence times, taking wide range of A_O and B_O. The values of A were calculated from the temperature rise and known heat of reaction. Table 7, Appendix B presents the values of

$$-\frac{2.303}{(B_O-A_O)}\left[\log\frac{A}{A+(B_O-A_O)}\right]_{A_O}^{A}$$ and k'' for each residence

time for various runs.

Figure 5 shows a plot of the left hand side of equation (4) versus θ. As seen in Figure 5, the experimental data are well correlated by a straight line indicating that the reaction between hypochlorite and sulfite is an irreversible second order reaction.

Error bars[a], based on the small errors in the concentration and temperature measurements are included. The value of the

[a]Error bars are equal to twice the standard deviation.
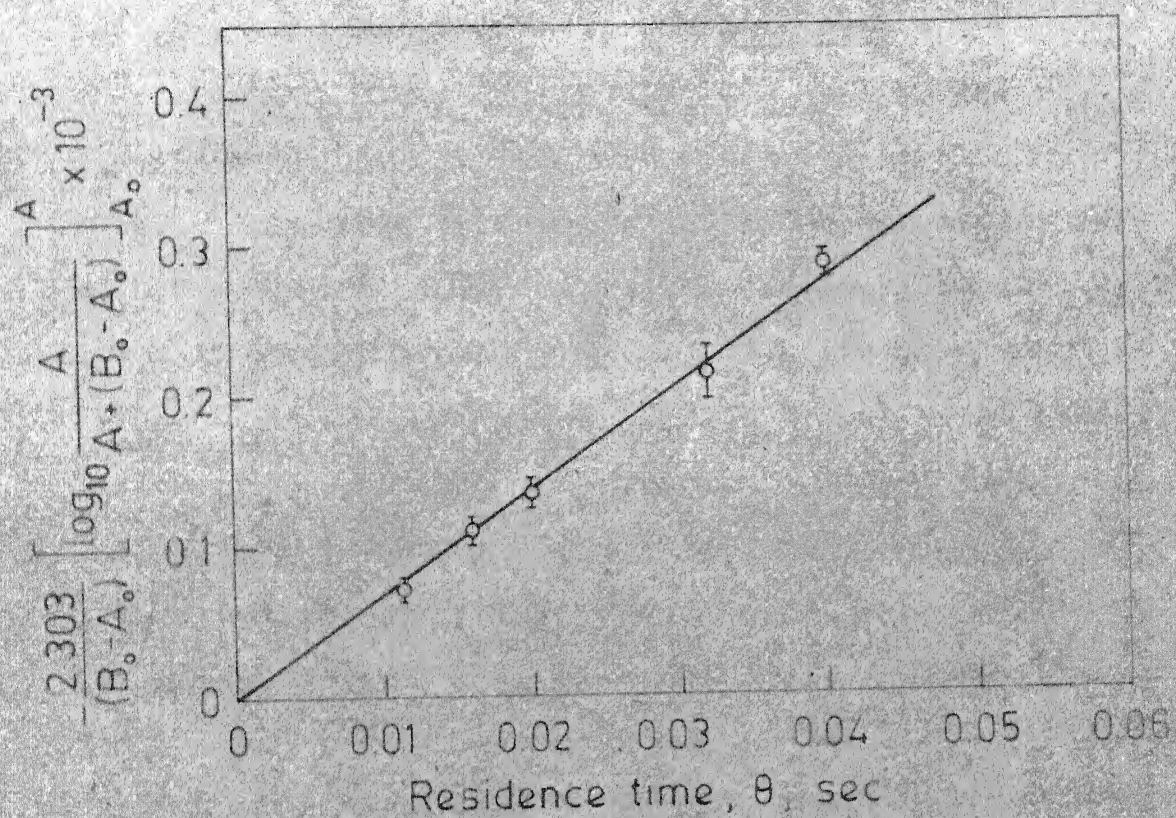
Fig 5 Integral analysis of experimental data

second order rate constant k" was calculated from the slope
of this straight line. The value of k" at 30°C was found to
be 6750 (lit)/(gmole)(sec).

3.4 Effect of temperature on reaction rate

To observe the effect of temperature on the rate of
the reaction, experiments were conducted at 21, 30, 35, and
40°C. The hypochlorite and sulfite concentrations were fixed
at 0.00125 M and 0.00375 M, respectively. The rate data are
given in Tables 5 and 6, Appendix B. The rate constant k"
for each temperature was calculated at different residence
times. Table 8, Appendix B, presents values of k".

Figure 6 shows a plot of the logarithm of k" versus
inverse of absolute temperature. Data of Lister and Rosenblum
[6] are also plotted in Figure 6. It is evident from this
figure that the value of k" agrees with those reported by
Lister and Rosenblum at 40°C. The apparent activation energy
for the overall reaction was calculated to be 15.6 kcal/gmole.
This value is typical of the values for homogeneous reactions
[16], however, it is approximately twice the value reported by
Lister and Rosenblum [6].

Data on the heats of formation of the compounds (in
aqueous solution) in the reaction

$$NaOCl + H_2O \longrightarrow HOCl + NaOH$$
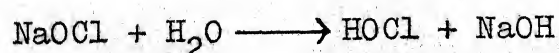
make the heat of hydrolysis of the hypochlorite ion to be
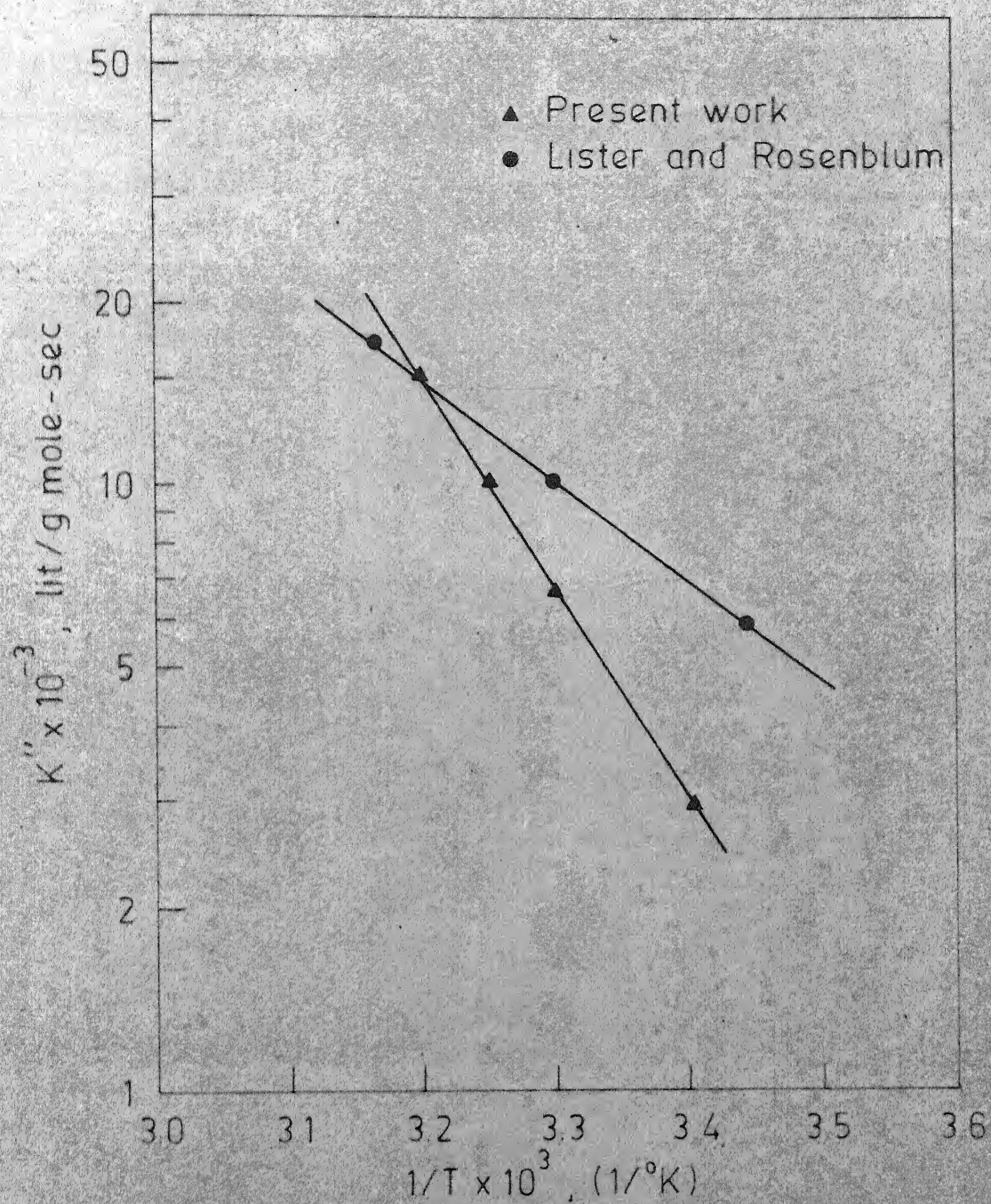
Fig 6 Effect of temperature on reaction rate constant

11.0 kcal/gmole. The energy of activation for the reaction of sulfite ions and hypochlorous acid would then only be 4.6 kcal/gmole if the reaction proceeded with HOCl rather than OCl$^-$. This will be unlikely since the reactions of this type have the activation energy greater than 10 kcal/gmole.

CHAPTER 4

CONCLUSIONS

The kinetics of the reaction of sodium hypochlorite and sodium sulfite have been studied by the rapid-mixing method of Hartridge and Roughton. The experimental results showed that the reaction rate was first order with respect to both the hypochlorite and the sulfite concentrations. Both the differential and integral analysis of the data were made. The experimental data were correlated with the second order rate expression and the value of second order rate constant at $30^{\circ}C$ was calculated to be 6750 liter/gmole sec. The apparent activation energy for the overall oxidation-reduction was calculated to be 15.6 kcal/gmole.

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A P P E N D I X - A

CALIBRATION OF THERMOCOUPLES

APPENDIX   A

CALIBRATION OF THERMOCOUPLES

The thermocouples were made and calibrated against a 25 ohm Leeds and Northrup platinum resistance thermometer and Muller bridge assembly. The details of the apparatus and procedure are given elsewhere [17].

Figure 7 is the plot of the microvoltmeter output (mV) versus temperature difference ($^{\circ}$C) at datum temperature of 30°C. Using L.M.S. curve fit the following relation was obtained.

$$(Output)_{m.V.} = 0.6366 \times (Temperature\ difference,\ ^{\circ}C)$$
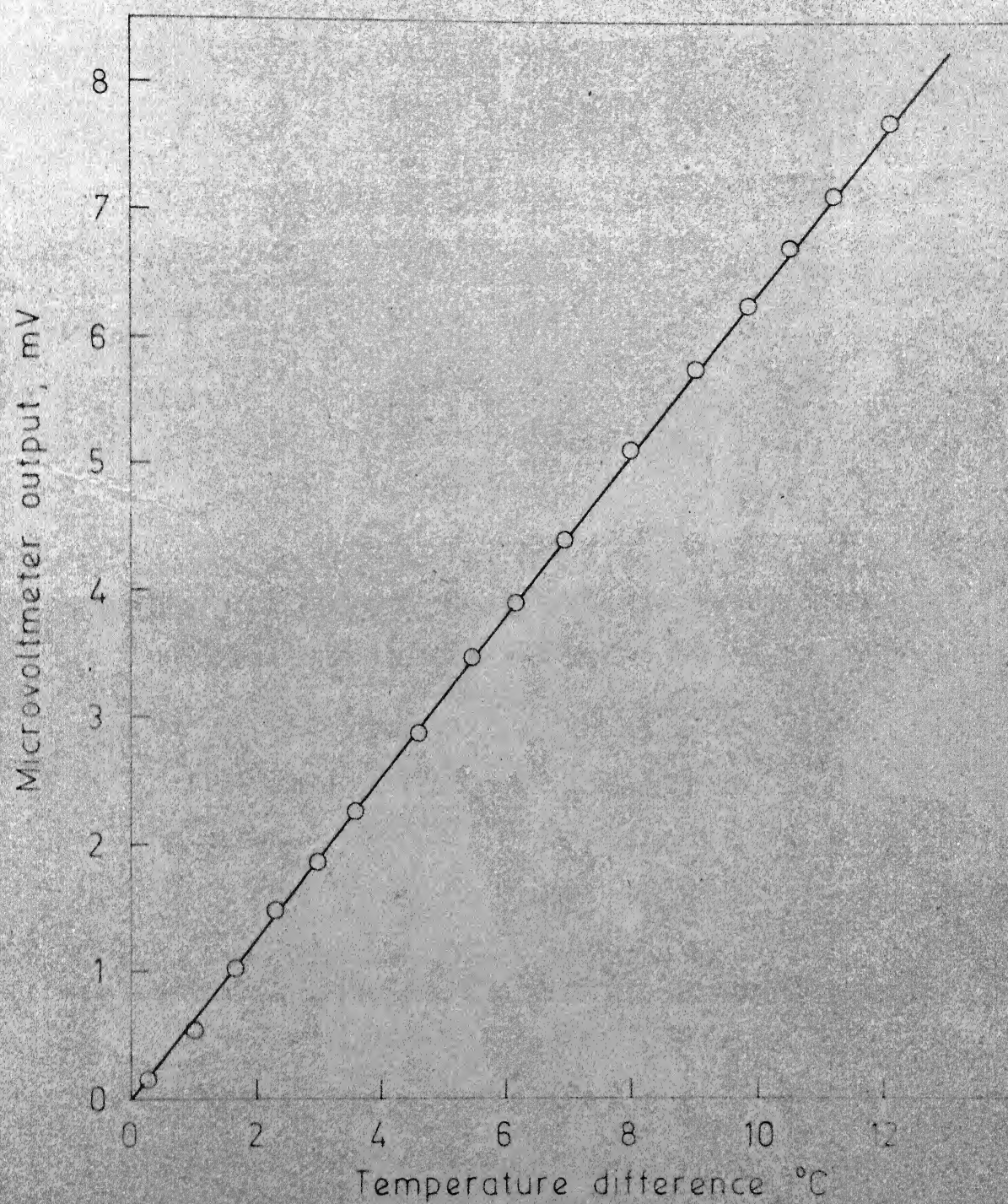
Fig 7 Calibration curve for thermocouples at

APPENDIX B

RECORDED AND CALCULATED DATA FOR THE REACTION BETWEEN
HYPOCHLORITE AND SULPHITE

TABLE 1: RECORDED DATA FOR EFFECT OF HYPOCHLORITE CONCENTRATION

Reaction Temperature = 30°C

Run No.	Stock Solution Conc. of sulphite (M)	Conc. of hypochlorite (M)	Volume of Reactor (c.m.^{3})	Flow rate of sulphite solution (ml/sec)	Flow Rate of hypochlorite solution (ml/sec)	Microvoltmeter output (m.V.)
1	2	3	4	5	6	7
RH-1	0.005	0.00125	0.16	7.0	7.0	0.005
			0.16	2.5	2.5	0.0125
			0.16	2.0	2.0	0.0160
RH-2	0.005	0.0025	0.16	7.0	7.0	0.0085
			0.16	4.0	4.0	0.0150
			0.16	2.0	2.0	0.0300
RH-3	0.005	0.00375	0.16	7.0	7.0	0.0120
			0.16	4.0	4.0	0.0220
			0.16	2.5	2.5	0.0350
RH-4	0.005	0.005	0.16	7.0	7.0	0.0160
			0.16	5.0	5.0	0.0230
			0.16	4.0	4.0	0.0300
			0.16	2.0	2.0	0.0610
RH-5	0.005	0.0075	0.16	7.0	7.0	0.0280
			0.16	5.0	5.0	0.0400
			0.16	4.0	4.0	0.0470

Table 1 (contd)

1	2	3	4	5	6	7
RH-6	0.005	0.01	0.16	7.0	7.0	0.0370
			0.16	5.0	5.0	0.0490
			0.16	4.0	4.0	0.0590
RH-7	0.0150	0.00125	0.16	7.0	7.0	0.0140
			0.16	5.0	5.0	0.0170
			0.16	4.0	4.0	0.0200
			0.16	2.5	2.5	0.0260
RH-8	0.0150	0.0025	0.16	7.0	7.0	0.0230
			0.16	4.0	4.0	0.0400
			0.16	2.5	2.5	0.0725
RH-9	0.0150	0.005	0.16	7.0	7.0	0.0620
			0.16	5.0	5.0	0.0750
			0.16	4.0	4.0	0.0850
			0.16	2.5	2.5	0.1050
RH-10	0.00150	0.0075	0.16	7.0	7.0	0.0750
			0.16	5.0	5.0	0.1100
			0.16	4.0	4.0	0.1200
			0.16	2.5	2.5	0.1430

TABLE 2: CALCULATED DATA FOR EFFECT OF HYPOCHLORITE CONCENTRATION

Reaction Temperature = 30°C

Run No.	In Reactor Average sulphite conc.(M)	Average Hypochlorite conc.(M)	Total flow Rate (ml/sec)	Residence Time (sec)	Rise in Temperature(°C)	Reaction Rate (M/sec)
1	2	3	4	5	6	7
RH-1	0.0025	0.00063	14.0	0.01143	0.007832	7.55×10^{-3}
			5.0	0.03200	0.01958	
			4.0	0.04000	0.02506	
RH-2	0.0025	0.00125	14.0	0.01143	0.01331	14.45×10^{-3}
			8.0	0.02000	0.02349	
			4.0	0.04000	0.04699	
RH-3	0.0025	0.00188	14.0	0.01143	0.01879	23.21×10^{-3}
			8.0	0.02000	0.03446	
			5.0	0.03200	0.05482	
RH-4	0.0025	0.0025	14.0	0.01143	0.02506	29.16×10^{-3}
			10.0	0.01600	0.03602	
			8.0	0.02000	0.04699	
			4.0	0.04000	0.09554	
RH-5	0.0025	0.00375	14.0	0.01143	0.04386	46.21×10^{-3}
			10.0	0.01600	0.06265	
			8.0	0.02000	0.07362	

Table 2 (contd)

1	2	3	4	5	6	7
RH-6	0.0025	0.005	14.0	0.01143	0.05795	57.38×10^{-3}
			10.0	0.01600	0.07675	
			8.0	0.02000	0.09241	
RH-7	0.0075	0.00063	14.0	0.01143	0.02193	20.55×10^{-3}
			10.0	0.01600	0.02663	
			8.0	0.02000	0.03133	
			5.0	0.03200	0.04072	
RH-8	0.0075	0.00125	14.0	0.01143	0.04386	41.42×10^{-3}
			8.0	0.02000	0.06265	
			5.0	0.03200	0.11356	
RH-9	0.0075	0.0025	14.0	0.01143	0.09711	96.32×10^{-3}
			10.0	0.01600	0.11722	
			8.0	0.02000	0.13313	
			5.0	0.03200	0.16446	
RH-10	0.0075	0.000375	14.0	0.01143	0.11747	135.98×10^{-3}
			10.0	0.01600	0.17229	
			8.0	0.02000	0.18795	
			5.0	0.03200	0.22398	

TABLE 3: RECORDED DATA FOR EFFECT OF SULPHITE CONCENTRATION

Reaction Temperature = $30^{\circ}C$

Run No.	Stock Solution		Volume of Reactor (cm³)	Flow rate of sulphite solution (ml/sec)	Flow rate of hypochlorite solution (ml/sec)	Microvoltmeter output (m.V.)
	Conc. of sulphite (M)	Conc. of Hypochlorite (M)				
1	2	3	4	5	6	7
RS-1	0.0025	0.0025	0.16	7.0	7.0	0.0045
			0.16	4.0	4.0	0.0075
			0.16	2.5	2.5	0.0120
RS-2	0.005	0.0025	0.16	7.0	7.0	0.0085
			0.16	4.0	4.0	0.0150
			0.16	2.0	2.0	0.0300
RS-3	0.0075	0.0025	0.16	7.0	7.0	0.0110
			0.16	4.0	4.0	0.0215
			0.16	2.5	2.5	0.0320
RS-4	0.010	0.0025	0.16	7.0	7.0	0.0180
			0.16	4.0	4.0	0.0310
			0.16	2.5	2.5	0.0480
			0.16	2.0	2.0	0.0500
RS-5	0.015	0.0025	0.16	7.0	7.0	0.0230
			0.16	4.0	4.0	0.0400
			0.16	2.5	2.5	0.0725

Table 3 (contd)

1	2	3	4	5	6	7
RS-6	0.020	0.0025	0.16	7.0	7.0	0.0320
			0.16	5.0	5.0	0.0430
			0.16	4.0	4.0	0.0500
RS-7	0.0025	0.0125	0.16	7.0	7.0	0.0170
			0.16	5.0	5.0	0.0250
			0.16	4.0	4.0	0.0380
RS-8	0.005	0.0125	0.16	7.0	7.0	0.0410
			0.16	5.0	5.0	0.0615
			0.16	4.0	4.0	0.0700
RS-9	0.010	0.0125	0.16	7.0	7.0	0.0630
			0.16	5.0	5.0	0.1090
			0.16	4.0	4.0	0.1310
RS-10	0.015	0.0125	0.16	7.0	7.0	0.1130
			0.16	5.0	5.0	0.1635

TABLE 4: CALCULATED DATA FOR EFFECT OF SULPHITE CONCENTRATION

Reaction Temperature = 30°C

Run No.	In Reactor Average Sulphite Conc. (M)	Average Hypochlorite Conc. (M)	Total Flow Rate (ml/sec)	Residence Time (sec)	Rise in Temperature (°C)	Reaction Rate (M/sec)
1	2	3	4	5	6	7
RS-1	0.00125	0.00125	14.0	0.01143	0.00705	7.22×10^{-3}
			8.0	0.02000	0.01175	
			5.0	0.03200	0.01880	
RS-2	0.0025	0.00125	14.0	0.01143	0.01331	14.44×10^{-3}
			8.0	0.02000	0.02349	
			4.0	0.04000	0.04699	
RS-3	0.00375	0.00125	14.0	0.01143	0.01723	23.21×10^{-3}
			8.0	0.02000	0.03368	
			5.0	0.03200	0.05012	
RS-4	0.005	0.00125	14.0	0.01143	0.02819	29.38×10^{-3}
			8.0	0.02000	0.04855	
			5.0	0.03200	0.07518	
			4.0	0.04000	0.07782	
RS-5	0.0075	0.00125	14.0	0.01143	0.04386	41.70×10^{-3}
			8.0	0.20000	0.06265	
			5.0	0.32000	0.11356	

Table 4 (contd)

1	2	3	4	5	6	7
RS-6	0.0100	0.00125	14.0	0.01143	0.05012	57.79×10^{-3}
			10.0	0.01600	0.06735	
			8.0	0.02000	0.07831	
RS-7	0.00125	0.00625	14.0	0.01143	0.02663	32.68×10^{-3}
			10.0	0.01600	0.03916	
			8.0	0.02000	0.05952	
RS-8	0.0025	0.00625	14.0	0.01143	0.06422	71.27×10^{-3}
			10.0	0.01600	0.09633	
			8.0	0.02000	0.10964	
RS-9	0.005	0.00625	14.0	0.01143	0.09868	125.21×10^{-3}
			10.0	0.01600	0.17073	
			8.0	0.02000	0.20519	
RS-10	0.0075	0.00625	14.0	0.01143	0.17699	211.90×10^{-3}
			10.0	0.01600	0.25609	

TABLE 5: RECORDED DATA FOR EFFECT OF TEMPERATURE ON REACTION RATE

Run No.	Temp., °C	Stock Solution		Volume of Reactor (cm^{-3})	Flow Rate of Sulphite Solution (ml/sec)	Flow Rate of Hypochlorite Solution (ml/sec)	Microvoltmeter Output (m.V.)
		Conc. of Sulphite Solution (M)	Conc. of Hypochlorite Solution (M)				
RT-1	21	0.0075	0.0025	0.16	7.0	7.0	0.0080
				0.16	5.0	5.0	0.0095
				0.16	4.0	4.0	0.0125
				0.16	2.5	2.5	0.0180
				0.16	2.0	2.0	0.0220
RT-2	30	0.0075	0.0025	0.16	7.0	7.0	0.0110
				0.16	4.0	4.0	0.0215
				0.16	2.5	2.5	0.0340
RT-3	40	0.0075	0.0025	0.16	7.0	7.0	0.0300
				0.16	5.0	5.0	0.0370
				0.16	4.0	4.0	0.0410

TABLE 6: CALCULATED DATA FOR EFFECT OF TEMPERATURE ON REACTION RATE

Run No.	Temp., °C	In Reactor		Total Flow Rate (ml/sec)	Residence Time (sec)	Rise in Temperature, (°C)	Reaction Rate (M/sec)
		Average Sulphite Conc.(M)	Average Hypochlorite Conc. (M)				
RT-1	21	0.00375	0.00125	14.0	0.01143	0.01253	10.6×10^{-3}
				10.0	0.01600	0.01487	
				8.0	0.02000	0.01958	
				5.0	0.03200	0.02819	
				4.0	0.04000	0.03446	
RT-2	30	0.00375	0.00125	14.0	0.01143	0.01723	23.2×10^{-3}
				8.0	0.02000	0.03368	
				5.0	0.03200	0.05325	
RT-3	40	0.00375	0.00125	14.0	0.01143	0.04698	55.7×10^{-3}
				10.0	0.01600	0.05795	
				8.0	0.02000	0.06422	

TABLE 7: VALUES OF k" AND OTHER PARAMETERS

Reaction Temperature = 30°C

S.No.	$[OCl^-]$ $B_0 \times 10^3$ (M)	$[SO_3^-]$ $A_0 \times 10^3$ (M)	Residence Time $\theta \times 10^3$ (sec)	$-\frac{2.303}{(B_0-A_0)}\left[\log \frac{A}{A+(B_0-A_0)}\right]_{A_0}^{A} \times 10^{-3}$	Standard Deviation (s.d.) (per cent)	k" $(gmole/lit)^{-1}sec^{-1}$
1	0.63	2.5	11.43	0.0653		5713
2	1.25	2.5	11.43	0.0580		5074
3	3.75	2.5	11.43	0.0702		6142
4	5.0	2.5	11.43	0.0727		6360
5	0.63	7.5	11.43	0.0759		6648
6	1.25	7.5	11.43	0.0784		6860
7	3.75	7.5	11.43	0.0727		6360
8	1.25	5.0	11.43	0.0675		5906
9	1.25	10.0	11.43	0.0703		6150
10	6.25	7.5	11.43	0.0683	s.d.=0.006 Per cent = 8.4	5976
11	3.75	2.5	16.00	0.1107		6918
12	5.00	2.5	16.00	0.1059		6619
13	0.63	7.5	16.0	0.1003		6268
14	3.75	7.5	16.0	0.1068		6677
15	1.25	10.0	16.0	0.1143		7140
16	6.25	2.5	16.0	0.1146		7162
17	6.25	5.0	16.0	0.1082	s.d.=0.0075 Per cent =6.8	6762
18	6.25	7.5	16.0	0.1253		7831

Table 7 (contd)

1	2	3	4	5	6	7
19	1.25	2.5	20.0	0.1120		5600
20	1.88	2.5	20.0	0.1122		5610
21	3.75	2.5	20.0	0.1387		6935
22	5.00	2.5	20.0	0.1394		6970
23	1.25	7.5	20.0	0.1360		6798
24	3.75	7.5	20.0	0.1512		7560
25	1.25	3.75	20.0	0.1142		5710
26	1.25	5.0	20.0	0.1377		6885
27	1.25	10.0	20.0	0.1566		7832
28	6.25	1.25	20.0	0.1512		7560
29	6.25	2.5	20.0	0.1419	s.d.=0.0158	7095
30	6.25	5.0	20.0	0.1484	Per cent = 11.7	7420
31	0.63	2.5	32.0	0.2050		6406
32	1.88	2.5	32.0	0.2095		6547
33	0.63	7.5	32.0	0.2272		7099
34	3.75	7.5	32.0	0.2316	s.d.=0.0195	7238
35	1.25	3.75	32.0	0.1999	Per cent = 9.1	6247
36	0.63	2.5	40.0	0.2889	s.d.=0.0019	7223
37	1.25	2.5	40.0	0.2861	Per cent =0.66	7152

Average   6661

TABLE 8: VALUES OF k" AT DIFFERENT TEMPERATURES

Run No.	Reaction Temp., (°C)	Residence Time $\theta \times 10^3$ (sec)	Conc. of Sulphite at Time θ, $A \times 10^3$	$\dfrac{2.303}{(B_0-A_0)}\left[\log\dfrac{A}{A+(B_0-A_0)}\right]\dfrac{A_0}{A_0} \times 10^{-3}$	$k"$ $(gmole/lit)^{-1}(sec)^{-1}$
RT-1	21	11.43	3.5959	0.0359	3143
		16.00	3.5669	0.0434	2713
		20.00	3.5092	0.0589	2947
		32.00	3.4033	0.0912	2850
		40.00	3.3262	0.1176	2941
				Average	2918
RT-2	35	11.43	3.3551	0.1074	9387
		16.00	3.1721	0.1812	9060
		20.00	3.0565	0.2418	12090
		32.00	2.9794	0.2915	9108
				Average	9913
RT-3	40	11.43	3.1721	0.1812	15853
		16.00	3.0372	0.2536	15850
		20.00	2.9602	0.3051	15255
				Average	15652

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Sample calculation

Run No. RH-1

Reaction temperature = $30^{\circ}C$

$[OCl^-]$ = 0.00063 M

$[SO_3^{--}]$ = 0.0025 M

This run is plotted in Figure 2.

$$\Delta H_R \times M = \Delta T \times C_p$$

$$\frac{\Delta H_R \times M}{\Delta t} = \frac{\Delta T \times C_p}{\Delta t} = \frac{\Delta T}{\Delta t} \quad \text{as } C_p = 1.0$$

Reaction rate $= \dfrac{Slope}{\Delta H_R}$

Initial slope from Figure 2 = 0.6138

Reaction Rate $= \dfrac{0.6138}{81.31} = 7.55 \times 10^{-3}$ M/sec.

SECTION 2

REACTION OF CARBONDIOXIDE AND DIETHANOLAMINE

CONTENTS

NOMENCLATURE

A	concentration of CO_2, gmole/liter
A_o	initial concentration of CO_2, gmole/liter
B_o	initial concentration of DEA, gmole/liter
DEA	diethanolamine
k"	second order rate constant, $(\frac{gmole}{liter})^{-1}(sec)^{-1}$
M	concentration, gmoles/liter
T	absolute temperature, $^{\circ}K$
θ	time, sec

RUNS

RD	effect of DEA concentration
RC	effect of CO_2 concentration
RT	effect of temperature

LIST OF FIGURES

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CHAPTER 1

INTRODUCTION

1.1 General

Solutions of ethanolamines are used as powerful and rapid absorbing agents for removal of carbondioxide from mixtures of gases in many industrial processes. The frequent use of these solutions is because of their low volatility, thermal stability, high reactivity and the ease in regeneration of absorbing solutions. Some typical examples of its application are - removal of CO_2 from a mixture of H_2, N_2 and CO_2 in synthetic ammonia industry; upgrading of town gas, and natural gas; manufacture of methanol and synthetic gasolines; manufacture of solid CO_2, salicylic acid, carbonates and bicarbonates of sodium and potassium; and storage of fruit in controlled refrigerated atmospheres.

In most practical situations, the rate of absorption is influenced by the kinetics of the reaction between carbon dioxide and ethanolamine solution. Therefore, a knowledge of the kinetics of the reaction between carbondioxide and amine solution is important in the rational design of absorption equipment.

Although, the kinetics of these systems (CO_2 removal by monoethanolamine, diethanolamine, and triethanolamine) have been investigated by many workers, considerable

discrepancies exist for the reaction between carbondioxide and diethanolamine solutions. It is essentially in regard to clarify the kinetics of diethanolamine-carbondioxide reaction, the present work was carried out. The resulting information, however, remains inconclusive due to complex nature of the reaction.
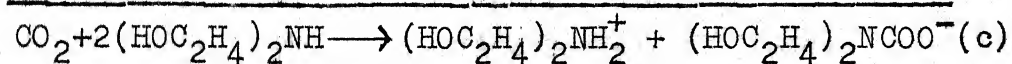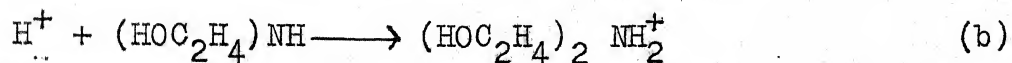
1.2 Literature survey

The earliest study of the reaction between CO_2 and diethanolamine (DEA) was conducted by Jensen, Jorgensen, and Fourholt [1]. Atmospheric air containing about 10 per cent CO_2 was led into solutions containing both amine and sodium hydroxide. The concentration of sodium hydroxide was varied from half to double the amine concentration. The authors observed that carbamate was the only reaction product and it decomposed to carbonate after several minutes. The second order rate constant reported at $18^{\circ}C$ was 5400(lit) /(gmole) (sec).

Jorgensen [2] studied the CO_2-DEA system using the same experimental technique as Jensen et al. [1] and also obtained a value for carbamate formation of 5400(lit) /(mole) (sec) at $18^{\circ}C$. However, he allowed the possibility of a competing reaction indicating that the reaction product formed was a mixture of carbamate and alkyle carbonate. In strongly alkaline solutions, the amount of alkyle carbonate

formed was excessive. Sodium hydroxide concentration was varied from one-third to three times the DEA concentration.

Nunge and Gill [3] studied the absorption of CO_2 into pure DEA in a gas-liquid stirred reactor at 85, 95, and 105°F. The absorption was followed by pressure-time measurements. An equation describing the gas-liquid absorption system was derived and then simplified by considering only kinetic region. The experimental data were correlated with this simplified equation and they indicated that the reaction follows a 3rd order equation: 1st order in CO_2 and 2nd order in DEA.

Sharma [4] studied the reaction between CO_2 and DEA and suggested that the reaction takes place according to the following mechanism:

$$CO_2 + (HOC_2H_4)_2 NH \longrightarrow (HOC_2H_4)_2 NCOO^- + H^+ \qquad (a)$$

$$H^+ + (HOC_2H_4) NH \longrightarrow (HOC_2H_4)_2 NH_2^+ \qquad (b)$$

$$CO_2 + 2(HOC_2H_4)_2NH \longrightarrow (HOC_2H_4)_2NH_2^+ + (HOC_2H_4)_2NCOO^- (c)$$
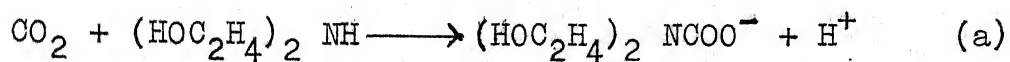
in which the first step reaction (a) is second order, i.e. first order with respect to both CO_2 and DEA, and is rate controlling [5]. The reaction proceeded to give amine salt of carbamic acid as the product of the reaction. The second order rate constant was found to be 1000, 1500 and 2500 $(\frac{gmole}{lit})^{-1}(sec)^{-1}$ at 18 , 25 , and 35°C, respectively. Sharma also reported that the contributions of the reactions with

water and hydroxyl ions to the overall rate of reaction were negligible under conditions used in practice for absorption of CO_2 in aqueous DEA solutions.
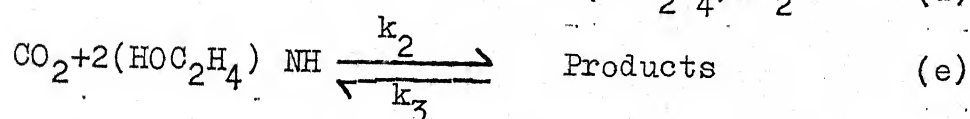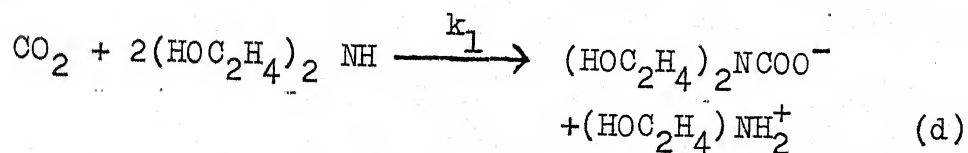
Leder [6] studied absorption of CO_2 in potassium carbonate-bicarbonate buffer solutions at high temperatures. The rates of absorption were catalysed by adding small amounts of water soluble amines. The second order rate constant for CO_2-DEA system was found to be 5556 $(\frac{gmole}{lit})^{-1}(sec)^{-1}$ at $19^\circ C$. The activation energy was calculated to be 10.5 kcal/gmole.

Hikita et al.[7] used rapid mixing method to study the kinetics of reaction of CO_2 with DEA solution. The overall reaction was observed to be third order, i.e. first order with respect to CO_2 and second order with respect to DEA. The experiments were conducted for short contact times (maximum of about 20 milliseconds). A constant heat of reaction was assumed without knowing its value either experimentally or from literature. The activation energy was found to be 12.7 kcal/gmole.

Sada et al. [8] carried out experiments over a wide range of contact times for the absorption of CO_2 into aqueous amine solutions. It was suggested from the experimental results with a laminarliquid-jet, a wetted wall column, and a quiescent liquid absorber that the present absorption processes should be analysed by a gas absorption with the consecutive reaction of the form of $A + 2B \xrightarrow{k_1} R$ and $A+R \xrightarrow{k_{II}}$ Products.

The value of the second order rate constant for the first reaction step (k_I) was estimated as 1340 $(gmole/lit)^{-1}(sec)^{-1}$ at $25^\circ C$. The k_{II} was estimated as $6.70 \times 10^{-2}(gmole/lit)^{-1}(sec)$.

Recently, Coldrey and Harris [9] studied the kinetics of the liquid phase reaction between CO_2 and diethanolamine by flow thermal method. The data indicated that the kinetics of the reaction is complex. The particular mechanism proposed consisted of two reactions which initially compete for the available carbondioxide. One of the these reactions was reversible, and regenerated carbondioxide as the overall reaction proceeded. Following is the reaction scheme proposed by these authors:

$$CO_2 + 2(HOC_2H_4)_2 NH \xrightarrow{k_1} (HOC_2H_4)_2NCOO^-$$
$$+(HOC_2H_4)NH_2^+ \qquad (d)$$

$$CO_2 + 2(HOC_2H_4) NH \underset{k_3}{\overset{k_2}{\rightleftharpoons}} \text{Products} \qquad (e)$$

The species participating in the proposed reversible reaction (e) were not identifiable from the data obtained. Apparent heat of reaction was also measured experimentally and it was found that it varied with the DEA concentration in the solution. The value of k_1 was obtained as $800(\frac{gmole}{lit})^{-1}$ $(sec)^{-1}$ at $18^\circ C$ and 11.66 kcal/gmole apparant heat of reaction.

The literature survey revealed that most kinetic studies of the reaction of CO_2 with DEA were made by absorbing gaseous carbondioxide directly into the amine. Despite the

considerable absorption data that exist for diethanolamine, most investigations of the kinetics result in conflicting conclusions. Even the two recent studies [7,9] by means of rapid flow technique resulted in entirely different conclusions.

The aim of the present work was therefore to study the rate of reaction between carbondioxide and diethanolamine directly, using the rapid mixing technique developed by Hartridge and Roughton [10].

1.3 Present work

The objective of this work has therefore been to study the kinetics of the homogeneous liquid phase reaction between carbondioxide and diethanolamine by means of flow thermal method. In this approach the experiment could be designed in such a way that the diffusion influence is negligible, and thus a true reaction kinetics can be established.

CHAPTER 2

EXPERIMENTAL APPARATUS AND PROCEDURE

2.1 Materials

The prime materials used herein were technical grade diethanolamine and carbondioxide. Diethanolamine was obtained from Amines and Chemicals Ltd., Bombay.

2.2 Apparatus

Rapid mixing continuous flow method of Hartridge and Roughton was used for the present study. The apparatus was similar to that used in Section 1.

2.3 Experimental procedure

Before each run, distilled water was charged to tank 2 and the carbondioxide was bubbled through the tank at a pressure for desired concentration for five to six hours to produce a carbondioxide solution. Diethanolamine solution was made by diluting the known amount of amine with distilled water, and was charged to tank 1. Both the solutions were allowed five to six hours to attain equilibrium. Amine solution was occasionally stirred with nitrogen.

Just prior to each run, both the solutions were analysed by standard titration methods. The carbondioxide concentration in the solution was determined by precipitating carbondioxide

as $BaCO_3$ using standard $Ba(OH)_2$ solution. The excess $Ba(OH)_2$ was then titrated with standard HCl to a neutral point. The determination of amine in solution was made by titrating the liquid sample with standard HCl using methyl orange as an indicator.

The experimental procedure for measuring the voltage rise was similar to that described in Section 1 (Chapter 2).

CHAPTER 3

RESULTS AND DISCUSSION

The experimental data have been presented in Appendix A. The energy liberated by reactions raised the temperature of the solution and the total temperature rise was measured. The change in carbondioxide concentration, M, was determined by the energy balance $H_R x M = T x C_p$. The mean heat capacity, C_p, of the solution was that of water since DEA concentration was low. Apparant heat of reaction, H_R, varied with the DEA concentration of the solution [9]. Figure 1 shows apparent heat of reaction as a function of DEA concentration.

3.1 Effect of reactants concentration

Figures 2 and 3 show the temperature profiles measured in the reactor as functions of DEA and CO_2 concentrations, respectively. It is obvious from these figures that first the temperature rises in the reactor with increase in residence time reaching to a maxima and then it drops to a minima. A further increase in residence time again increases the temperature rise. This type of behaviour was observed in all the runs. It is also evident from these figures that the reactant concentration has a considerable effect on the shape of the temperature profile. There is a prominent minimum in the profile at lower DEA or CO_2 concentration and this
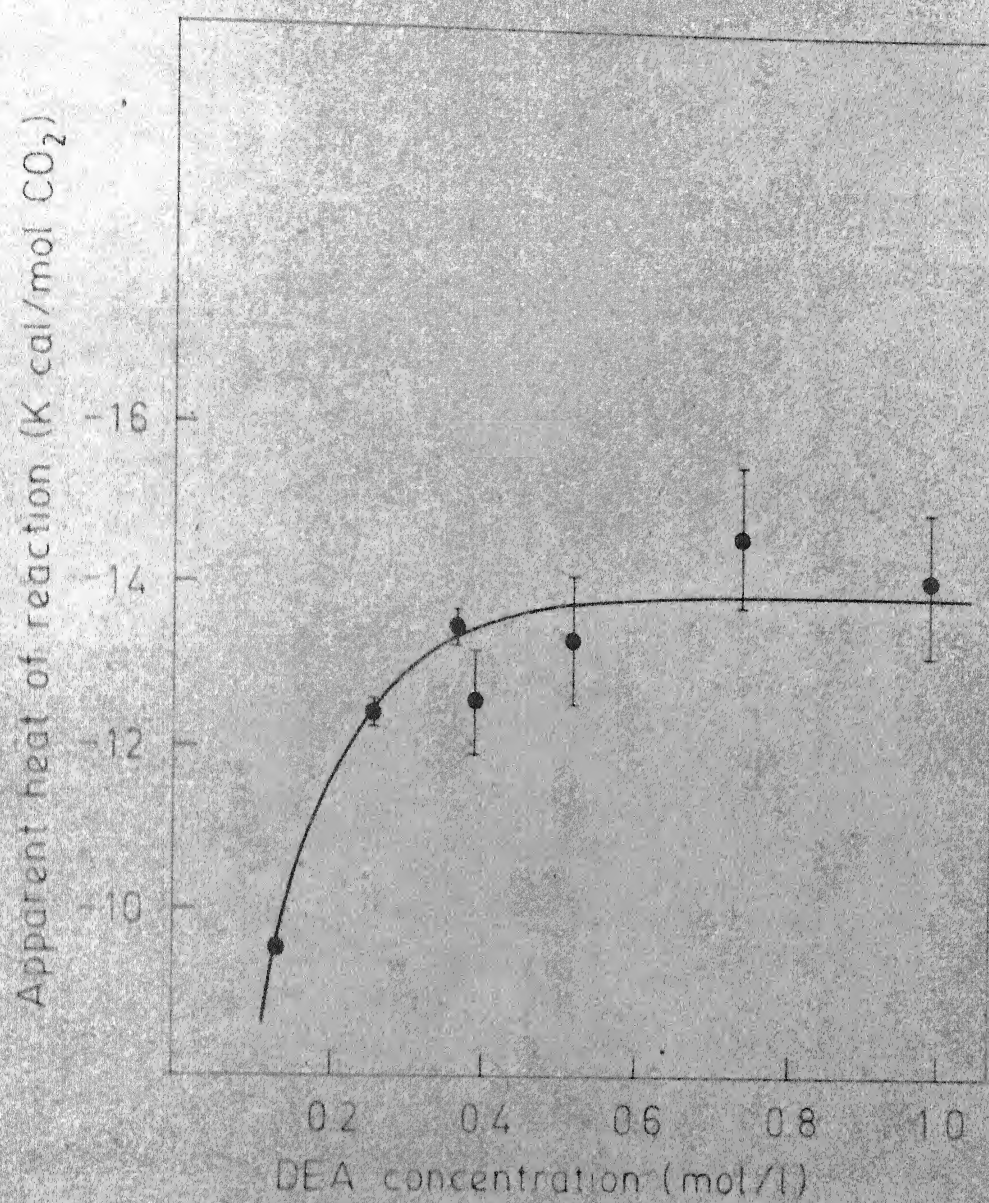
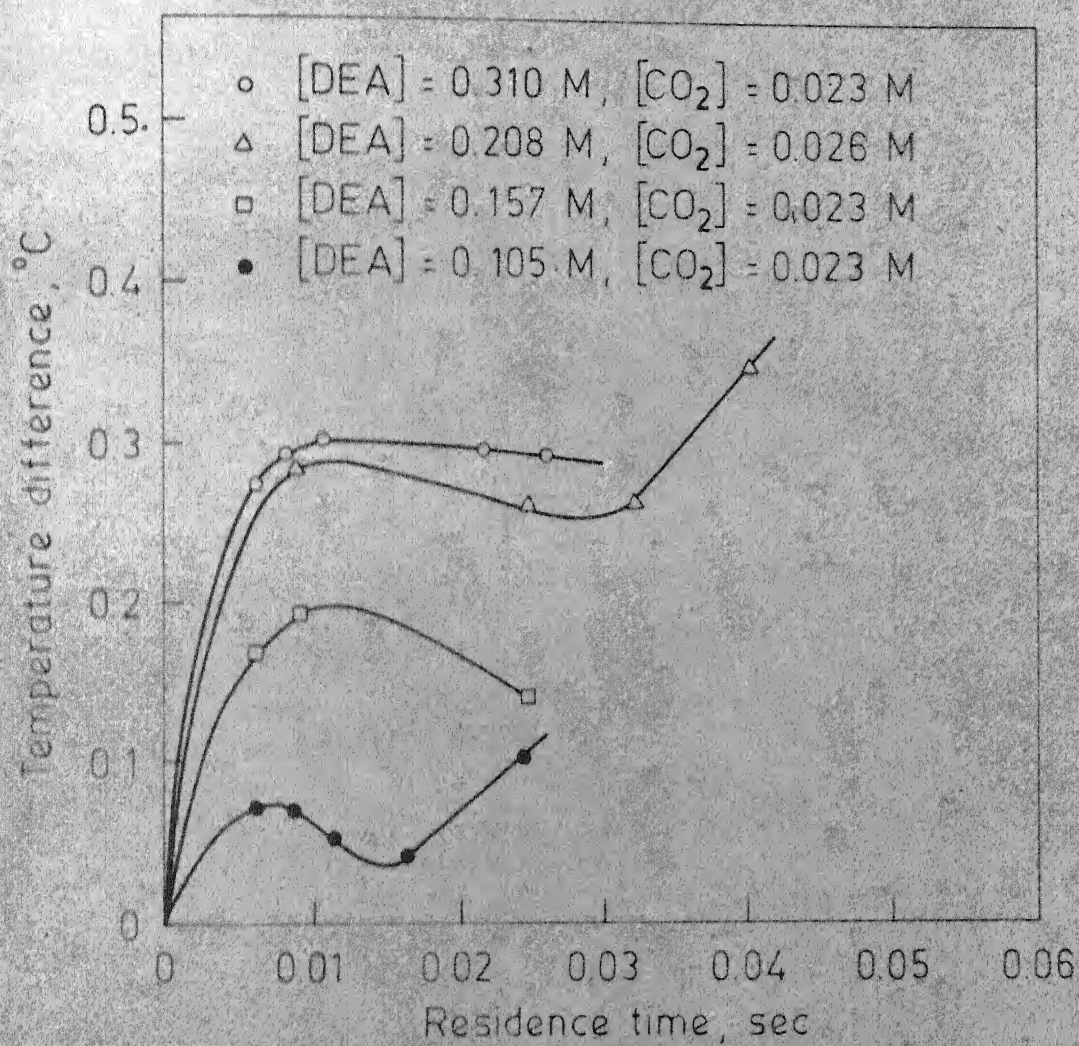Fig 1 Apparent heat of reaction for the CO_2/DEA
        system

Fig 2 Effect of DEA concentration
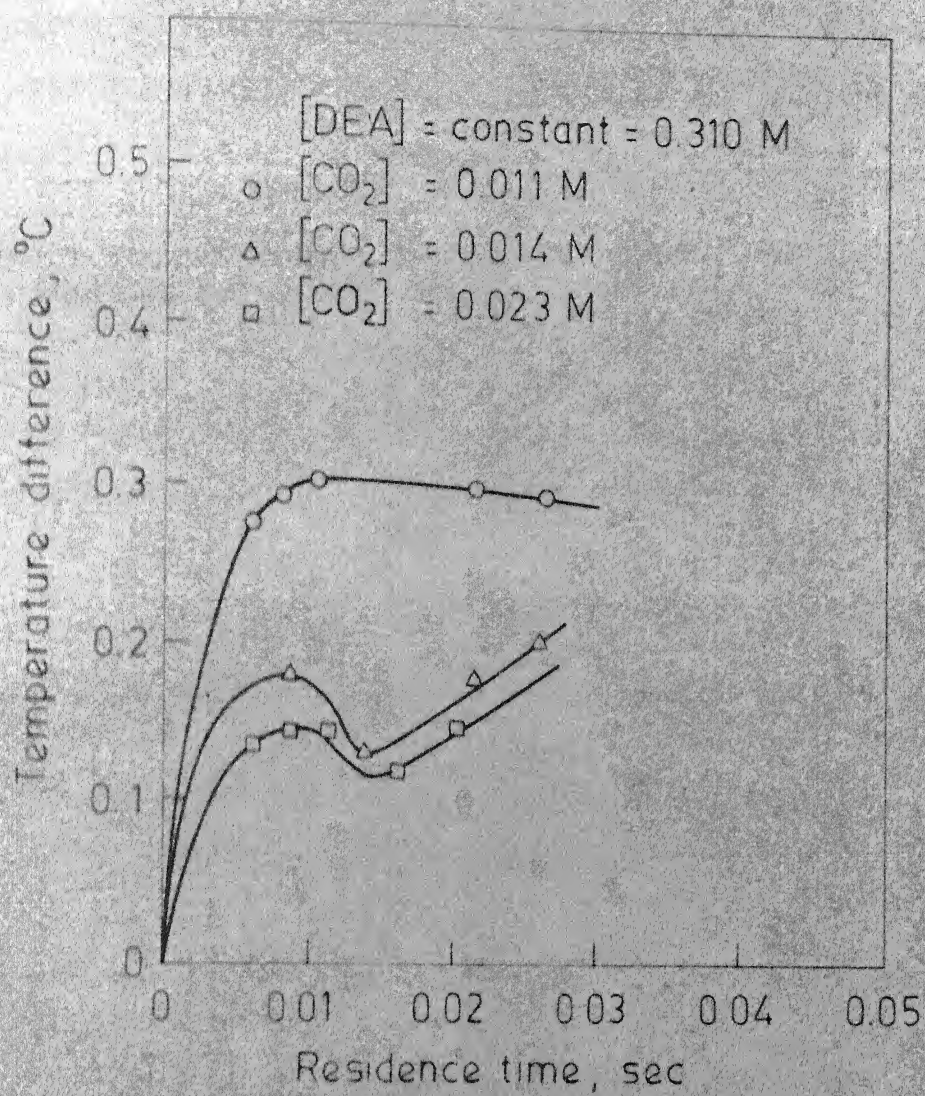
Fig 3 Effect of CO_2 concentration

becomes less significant as the concentrations are increased. A similar phenomena was observed by Coldrey and Harris [9] for CO_2-DEA system. The detailed experimental data are presented in Tables 2 through 5, Appendix A.

3.2 Effect of reactant temperature on profile

Effect of reactant temperature on temperature rise profile is shown in Figure 4. The temperature was varied in the range of 25 to $40^{\circ}C$. DEA concentration was kept constant at 0.208M. It is evident from this figure that the minimum is more significant at lower temperatures and becomes less prominent as the temperature is increased. The detailed data are presented in Tables 6 and 7, Appendix A.

3.3 Qualitative explanation of experimental data

The complex nature of the experimental data (Figures 2,3 and 4) obtained for the CO_2/DEA system indicates that there are several reaction processes occurring in the system simultaneously. Since the reaction of an amine with carbon-dioxide is evidently a simple second order process, as reported by several investigators [1,2,4,5,6,8], it appears that the alcohol groups of DEA are also involved, in some way, in the reaction of DEA with CO_2. Intramolecular bonds of the type -OH----N- have been observed by Bergman et al. [11] and DeRoos and Bakkar [12] in alkanolamines dissolved in organic solvents and interaction between hydroxyle and amine groups may be a factor affecting the reaction complexity.
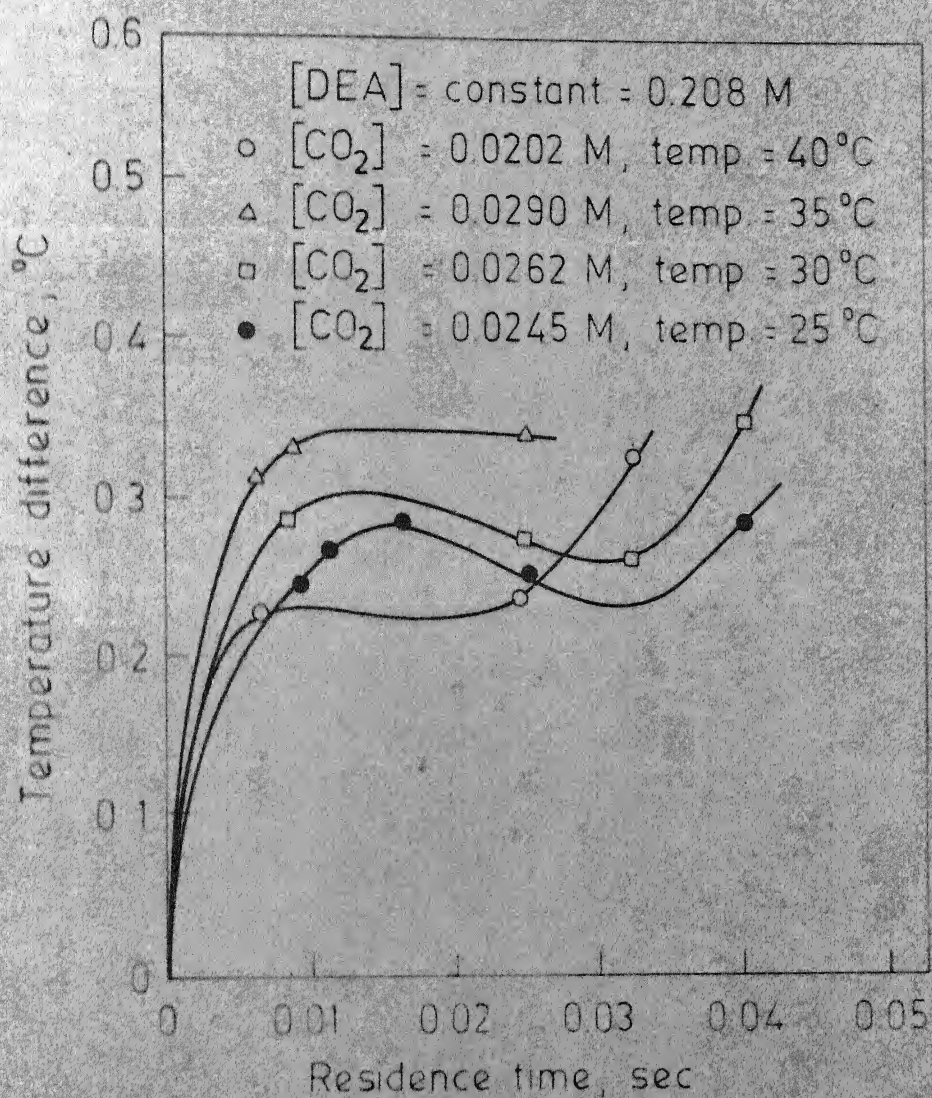
Fig 4   Effect of temperature

In order to explain experimentally determined temperature profiles it was assumed that the carbamate ion was one of the species formed and that it did not decompose in times shorter than the residence times of the reactants in the reactor. The formation of carbamate ion has been established by most investigators. The latter assumption was supported by Jorgensen [2] and Coldrey and Harris [9] by a simple chemical test. A temperature/time profile for the reaction of CO_2 with DEA, if the carbamate formation were the only reaction, would be similar to curve A on Figure 5. To explain the experimentally determined profile, curve C, it is necessary to assume that other reactions occur that produce temperature/time profile of the form represented by curve B. By adding the effects of the curves of the form of A and B, it is possible to produce qualitatively the shapes of the experimentally determined profiles. Certain information about the other reactions that occur, apart from carbamate formation, can be obtained from the nature of curve B. It can be concluded that the reaction producing the profile represented by curve B consist of a rapid exothermic reaction initially and this is followed by a rapid endothermic reaction that absorbs the heat liberated by the exothermic process.

Considering the nature of experimentally obtained temperature profiles and the above explanation, the following reaction scheme can be assumed.

Curve A   Temperature effect caused by
          carbamate formation reaction.
Curve B : Temperature effect caused by
          secondary reaction.
Curve C : Experimental profile

Curve C

Curve A

Curve B

Temperature rise in reactor

Residence time
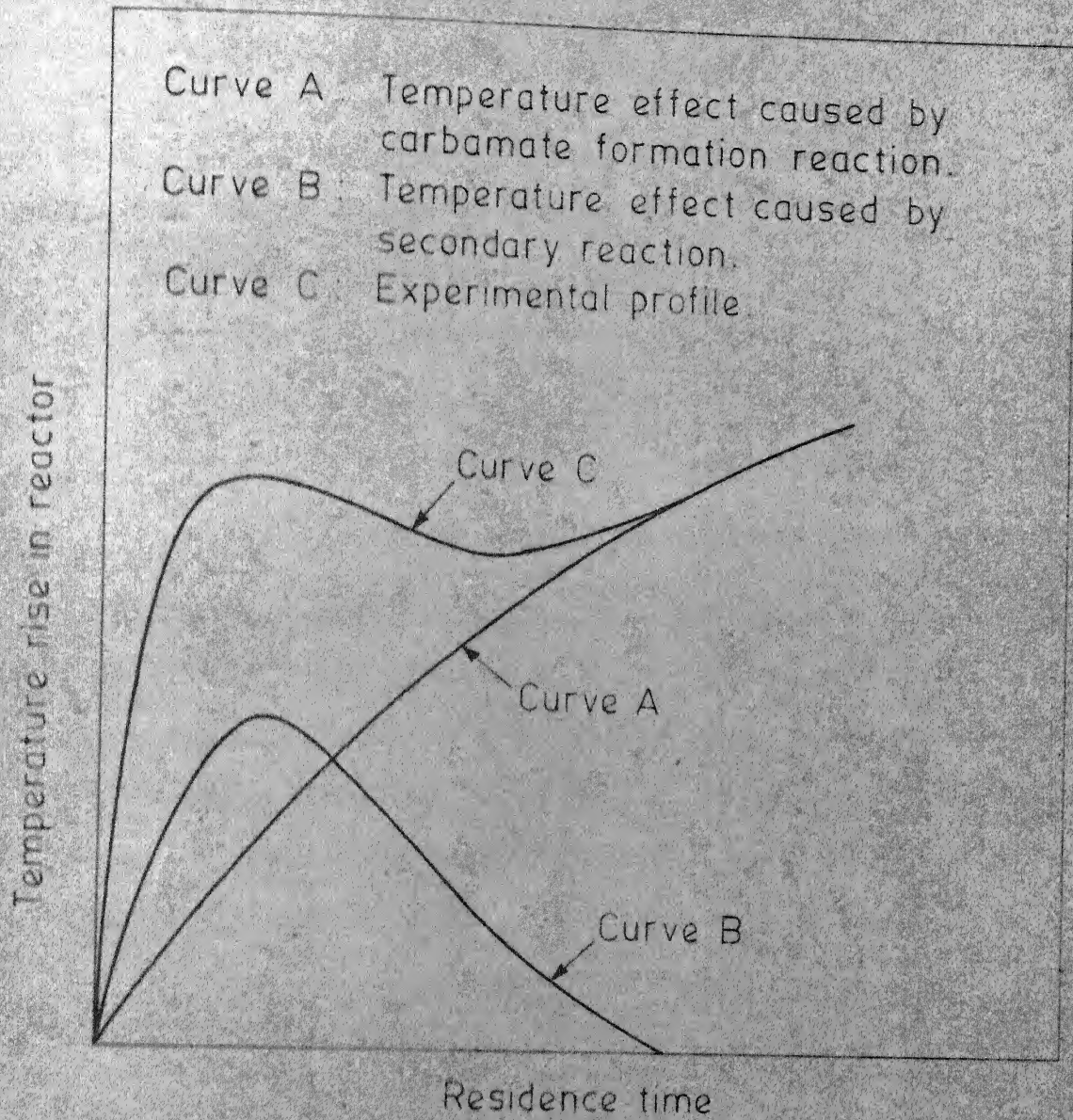
Fig 5   Theoretical explanation of the experimental profile

$$A + 2B \xrightarrow{k_1} C + R' \qquad \text{(d)}$$

$$A + 2F \underset{k_3}{\overset{k_2}{\rightleftharpoons}} \text{Products} \qquad \text{(e)}$$
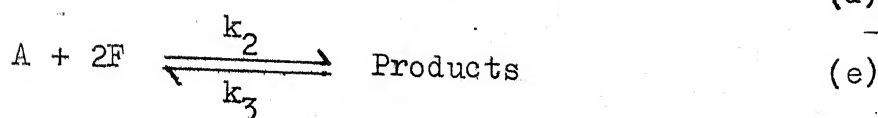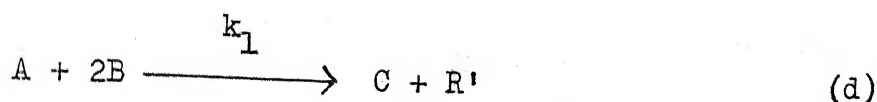
where

A = carbondioxide

B = NH (from DEA)

F = OH (from DEA)

C = Carbamate $[(HOC_2H_4)_2NCOO^-)]$

R' = Positively charged ion formed in carbamate

reaction $(R_2NH_2^+)$

Although the products of equation (e) have not been detected precisely, it is assumed that the alkyle carbonate formation and decomposition, or a process similar to that, is occurring in reaction (e). This assumption is reasonable as in a previous study Jorgensen [2] also reported the formation of alkyle carbonate.

3.4 Kinetics

From the nature of the experimentally measured profiles, it is very difficult to determine the complete kinetics of the system without knowing the products of reaction (e). Therefore, a study of the initial part of the temperature profile (i.e. before the maxima occures) was conducted in the present work.

If the overall reaction between DEA and CO_2 is irreversible and second order, as has been usually accepted in literature, for the initial part of the temperature profile, the following relationship should hold:

$$\frac{2.303}{B_0 - 2A_0} \left[\log \frac{A_0(2A + B_0 - 2A_0)}{A B_0} \right] = k'' \theta \qquad (1)$$

where A_0 and B_0 are initial concentrations of CO_2 and DEA respectively, A is the CO_2 concentration at any time θ and k'' is the second order reaction rate constant. Thus in this case, the value of k'' must be constant for different values of A_0, B_0 and θ at a constant temperature and pH.

The second order rate constants, k'', were calculated at $30^\circ C$ and a pH of 10.67 for different values of A_0, B_0, and θ, and it was found that the value was fairly constant giving an average k'' as 1823 $(\frac{gmole}{lit})^{-1}(sec)^{-1}$ with a standard deviation of 6 per cent. The detailed results are presented in Tables 8 and 9, Appendix A.

3.5 Apparent activation energy:

Figure 6 shows an Arrhenius plot of the values of the second order rate constant, k'', calculated from the experimental data. Experiments were conducted at 25, 30, 35, and $40^\circ C$. The apparant activation energy was found to be 12.41 kcal/gmole. The values obtained by several workers are given in Table 1.
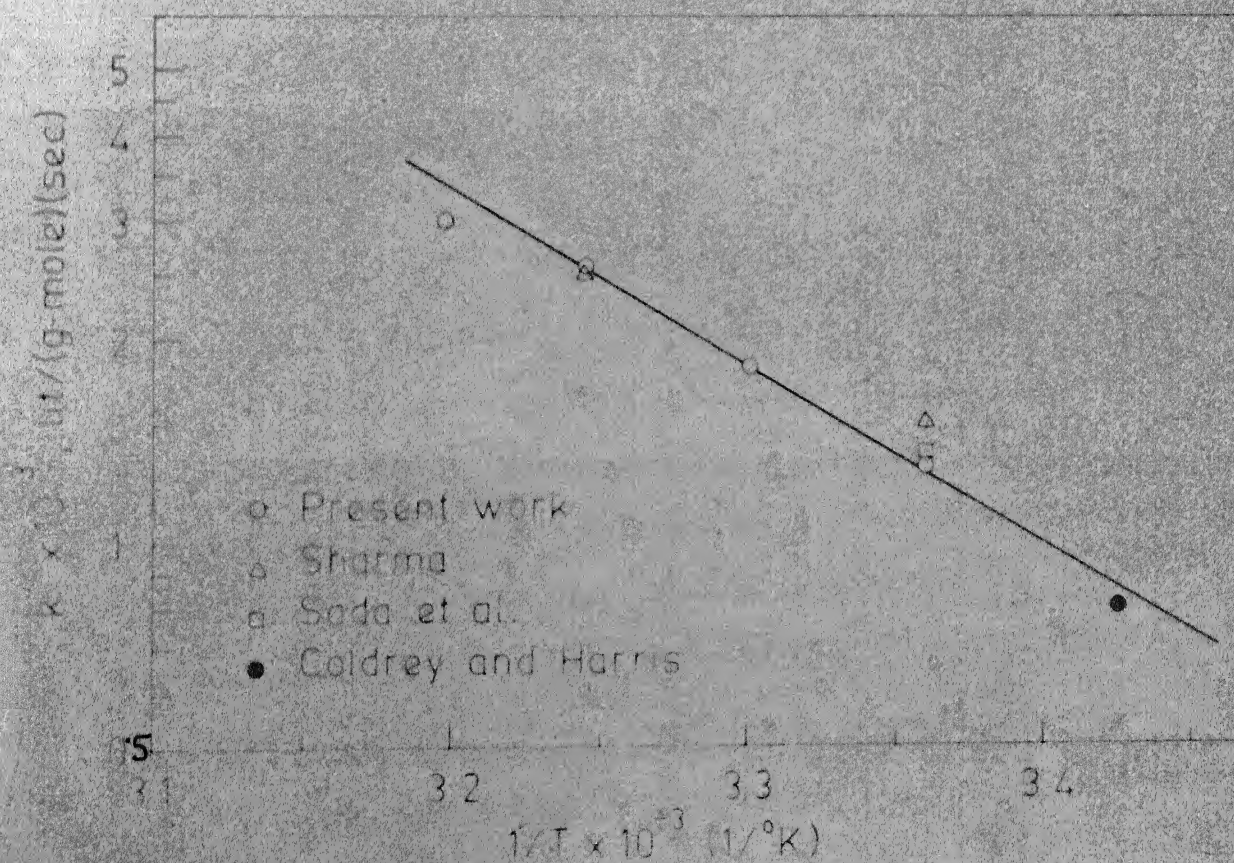
Fig. 6 Effect of temperature on k

TABLE 1: APPARANT ACTIVATION ENERGIES FOR CO_2-DEA SYSTEM PUBLISHED IN LITERATURE

Literature	E (kcal/gmole)
Sharma, et al.	9.98
Leder	10.50
Hikita et al.	12.70
Present work	12.41

The values of k" reported by Sharma [4], Sada et al. [8], and Coldrey and Harris (for carbamate formation taking H = -11.66 kcal/mole of DEA) [9] are also plotted in the same figure for comparison. It is evident from Figure 6 that these values are close to those obtained in the present work. The detailed results are presented in Table 10, Appendix A.

3.6 Comparison of results with other works

Jensen, Jorgensen, and Fourholt [1], and Jorgensen [2] obtained a much higher value of k" as 5400 $(\frac{gmole}{lit.})^{-1}(sec)^{-1}$ at 18°C. Experiments were conducted in strongly alkaline solutions with a pH of about 13. In an earlier paper [1], Jorgensen et al. reported that there is only carbamate formation reaction in the system. In another paper [2] Jorgensen reported that in highly alkaline solutions formation of alkyle carbonate was also occurred. But in both the works the amount of NaOH added was nearly same, so the agreement between the works of Jorgensen [2] and Jorgensen et al.[1]

is surprising. However, many of the observations of Jorgensen [2] are consistent with those of the present work. Points of agreement are:

1. There are two reactions which compete for the available CO_2: one of these being carbamate formation.

2. The products formed by these reactions are unstable, with the carbamate being considerably more stable than the other.

3. The carbamate formation reaction is favoured by an increase in temperature. (It is evident from Figure 4 as the minima becomes less prominant at higher temperatures).

The much higher value of k'' obtained in these works [1,2] can be explained due to the fact that the effective contact time between CO_2 and DEA was very low, so the rate constant predicted would be based on the initial part of the reaction in which CO_2 reacts more rapidly with NaOH.

Sharma [4] reported the formation of carbamate as the reaction product. The values of second order rate constant and activation energy reported by Sharma are in good agreement with those obtained in the present work. However, he did not observe the occurrence of the secondary reaction as concluded from the present work.

Hikita et al. [7] reported that the reaction was third order i.e. first order with respect to CO_2 and second order with respect to DEA. They performed their experiments for shorter residence times (maximum of about 20 milliseconds) and most experiments were conducted at higher DEA concentrations (more than 0.2 moles/liter). It is evident from the data obtained in the present work that the minima becomes less prominent as DEA concentration increases. Therefore, it appears that Hikital et al. might not be able to observe the nature of the temperature profiles (as obtained in the present work) at shorter residence times and higher DEA concentrations. Secondly, the authors assumed a constant heat of reaction without knowing its value either experimentally or from literature. In contrast to this, a variation of the apparant heat of reaction with DEA concentration have been reported in the literature [9]. Due to these reasons, the authors would have reached to a wrong conclusion giving a third order rate constant.

Sada et al. [8] suggested occurrence of a secondary reaction with the formation of carbamate reaction step. The second order rate constant for carbamate reaction step is in good agreement with those obtained in the present work.

CHAPTER 4

CONCLUSIONS

The study of the reaction kinetics of CO_2-DEA system was carried out by means of the rapid flow technique of Hartridge and Roughton. In this technique the diffusional resistances were eliminated by dissolving the CO_2 in distilled water.

The temperature profiles indicate that the reaction between CO_2 and DEA is complex. A reaction scheme was proposed consisting of two reactions, first reaction producing carbamate and a secondary reaction producing alkyle carbonate. The secondary reaction is reversible and as the overall reaction proceeds, the rate of its reverse process exceeds the forward rate so that some of the original reactants are regenerated.

For the initial part of the reaction, the overall second order rate constant and apparant activation energy were calculated and the results were compared.

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RECORDED AND CALCULATED DATA FOR THE REACTION
BETWEEN CARBONDIOXIDE AND DIETHANOLAMINE

TABLE 2: RECORDED DATA FOR EFFECT OF DEA CONCENTRATION

Reaction Temperature = $30^{o}C$; pH = 10.67

Run No.	Stock Solution		Heat of Reaction (H) (kcal/mole of DEA)	Volume of Reactor (cm^3)	Flow Rate of DEA Solution (ml/sec)	Flow Rate of CO_2 Solution (ml/sec)	Microvoltmeter Output (m.V.)
	Conc. of DEA Solution (M)	Conc. of CO_2 Solution (M)					
RD-1	0.2094	0.0454	5.0	0.16	13.3	13.3	0.0451
					9.0	9.0	0.0451
					7.0	7.0	0.0330
					5.0	5.0	0.0270
					3.25	3.25	0.0660
RD-2	0.3140	0.0440	10.0	0.16	13.3	13.3	0.1080
					9.0	9.0	0.1230
					3.25	3.25	0.0900
RD-3	0.4160	0.05246	11.66	0.16	10.0	10.00	0.1800
					3.25	3.25	0.1740
					2.50	2.50	0.1680
					2.00	2.00	0.2220
RD-4	0.9300	0.03485	13.00	0.16	8.75	17.5	0.176
					7.00	14.0	0.186
					5.00	10.0	0.192
					2.5	5.0	0.189
					2.0	4.0	0.186

TABLE 3: CALCULATED DATA FOR EFFECT OF DEA CONCENTRATION

Run No.	In Reactor		Total Flow Rate (ml/sec)	Residence Time (sec)	Rise in Temperature (°C)
	Conc. of DEA Solution (M)	Conc. of CO_2 Solution (M)			
RD-1	0.1047	0.0227	26.6	0.0060	0.07060
			18.0	0.0088	0.07060
			14.0	0.01143	0.05169
			10.0	0.0160	0.04229
			6.5	0.0246	0.10337
RD-2	0.1570	0.0220	26.6	0.0060	0.16916
			18.0	0.0088	0.19265
			6.5	0.0246	0.14097
RD-3	0.2080	0.02623	20.0	0.0080	0.28193
			6.5	0.0246	0.27254
			5.0	0.0320	0.26314
			4.0	0.0400	0.34772
RD-4	0.3100	0.02323	26.25	0.0060	0.27567
			21.0	0.0076	0.29133
			15.0	0.0106	0.30073
			7.5	0.0213	0.29603
			6.0	0.0266	0.29133

TABLE 4: RECORDED DATA FOR EFFECT OF CO_2 CONCENTRATION

Reaction Temperature = 30°C
pH = 10.67
Heat of Reaction = 13.0 kcal/mole of DEA [Ref.9]

Run No.	Stock Solution Conc. of DEA Solution (M)	Conc. of CO_2 Solution (M)	Volume of Reactor (cm³)	Flow Rate of DEA Solution (ml/sec)	Flow Rate of CO_2 Solution (ml/sec)	Microvoltmeter Output (m.V.)
RC-1	0.620	0.0220	0.16	13.3	13.3	0.0875
				9.0	9.0	0.0900
				7.0	7.0	0.0960
				5.0	5.0	0.0780
				4.0	4.0	0.0960
RC-2	0.465	0.0420	0.16	14.0	7.0	0.1140
				8.0	4.0	0.0840
				5.0	2.5	0.1140
				4.0	2.0	0.1260
RC-3	0.930	0.03485	0.16	8.75	17.5	0.1760
				7.00	14.0	0.1860
				5.00	10.0	0.1920
				2.5	5.0	0.1890
				2.0	4.0	0.1860

TABLE 5: CALCULATED DATA FOR EFFECT OF CO_2 CONCENTRATION

Run No.	In Reactor Conc. of DEA Solution (M)	Conc. of CO_2 Solution (M)	Total Flow Rate (ml/sec)	Residence Time (sec)	Rise in Temperature (°C)
RC-1	0.31	0.0110	26.6	0.0060	0.13731
			18.0	0.0088	0.14097
			14.0	0.01143	0.15036
			10.0	0.0160	0.12217
			8.0	0.0200	0.15036
RC-2	0.31	0.0140	21.0	0.0076	0.17856
			12.0	0.0133	0.13157
			7.5	0.0213	0.17856
			6.0	0.0266	0.19735
RC-3	0.31	0.02323	26.25	0.0060	0.27567
			21.0	0.0076	0.29133
			15.0	0.0106	0.30073
			7.5	0.0213	0.29603
			6.0	0.0266	0.29133

TABLE 6: RECORDED DATA FOR EFFECT OF TEMPERATURE ON REACTION RATE

pH = 10.67

Run No.	Temp., $^\circ$C	Stock Solution Conc. of DEA Solution (M)	Conc. of CO_2 Solution (M)	Volume of Reactor (cm^3)	Flow Rate of DEA Solution (ml/sec)	Flow Rate of CO_2 Solution (ml/sec)	Microvoltmeter Output (m.V.)
RT-1	25	0.416	0.0490	0.16	10.0	10.0	0.156
					7.0	7.0	0.168
					5.0	5.0	0.180
					3.25	3.25	0.162
					2.0	2.0	0.180
RT-2	30	0.416	0.05246	0.16	10.0	10.0	0.180
					3.25	3.25	0.174
					2.5	2.5	0.168
					2.0	2.0	0.222
RT-3	35	0.416	0.0580	0.16	13.3	13.3	0.200
					9.0	9.0	0.210
					3.25	3.25	0.216
RT-4	40	0.416	0.0404	0.16	13.3	13.3	0.144
					3.25	3.25	0.150
					2.50	2.50	0.207

TABLE 7: CALCULATED DATA FOR EFFECT OF TEMPERATURE ON REACTION RATE

Run No.	Temp., °C	In Reactor Average DEA concentration (M)	Average CO_2 concentration (M)	Total Flow Rate (ml/sec)	Residence Time (sec)	Rise in Temperature (°C)
RT-1	25	0.208	0.02450	20.0	0.008	0.02443
				14.0	0.01143	0.26314
				10.0	0.0160	0.28193
				6.5	0.0246	0.25374
				4.0	0.0400	0.28193
RT-2	30	0.208	0.02623	20.0	0.0080	0.28193
				6.5	0.0246	0.27254
				5.0	0.0320	0.26314
				4.0	0.0400	0.34772
RT-3	35	0.208	0.0290	26.6	0.0060	0.31338
				18.0	0.0088	0.32892
				6.5	0.0246	0.33832
RT-4	40	0.208	0.0202	26.6	0.0060	0.22554
				6.5	0.0246	0.23494
				5.0	0.032	0.32422

TABLE 8: VALUES OF k" AND OTHER PARAMETERS FOR EFFECT OF

DEA CONCENTRATION

Reaction Temperature = 30°C
pH = 10.67

Run No.	[DEA] (M) B_o	[CO_2] (M) A_o	Residence Time (sec)	$+ \dfrac{2.303}{(B_o-2A_o)}[\log \dfrac{A_o(2A+B_o-2A_o)}{A\,B_o}]$	k" (gmole/lit)$^{-1}$(sec)$^{-1}$
RD-1	0.1047	0.0227	0.006	11.1076	1851
RD-2	0.1570	0.0220	0.0050	16.0598	1825
				10.7820	1797
RD-3	0.2080	0.02623	0.0080	14.6812	1835
RD-4	0.3100	0.02323	0.0076	12.3444	1625
			0.0060	10.9923	1832
			0.01066	22.1235	2075

Average = 1834

TABLE 9: VALUES OF k" AND OTHER PARAMETERS FOR EFFECT OF CO_2 CONCENTRATION

Reaction Temperature = $30^{o}C$

pH = 10.67

H = 13.0 kcal/gmole of DEA

Run No.	[DEA] (M) B_o	[CO_2] (M) A_o	Residence Time (sec)	$\frac{2.303}{B_o-2A_o}\left[\log\frac{A_o(2A+B_o-2A_o)}{A\,B_o}\right]$	k" $(gmole/lit)^{-1}(sec)^{-1}$
RC-1	0.31	0.0110	0.0038	14.9526	1700
			0.0060	10.9501	1825
RC-2	0.31	0.0140	0.0076	14.0621	1850
RC-3	0.31	0.02323	0.0076	12.3444	1625
			0.0060	11.0112	1835
			0.0106	22.1295	2075

Average = 1818

TABLE 10: VALUES OF k" AND OTHER PARAMETERS FOR EFFECT OF TEMPERATURE

Run No.	Temp., (°C)	[DEA] (M) B_o	[CO$_2$] (M) A_o	Residence Time(sec) θ	$+ \dfrac{2.303}{(B_o - 2A_o)}\left[\log\dfrac{A_o(2A + B_o - 2A_o)}{(A - B_o)}\right]$	k" (gmole/lit)$^{-1}$ (sec)$^{-1}$
RT-1	25	0.208	0.02450	0.0080	10.8038	1350
				0.01143	14.5583	1273
					Average	1311
RT-2	30	0.208	0.02623	0.00800	14.6812	1835
RT-3	35	0.208	0.02900	0.0088	22.3104	2535
				0.0060	15.4381	2573
					Average	2554
RT-4	40	0.208	0.0202	0.0060	17.8606	2977

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